ARTIFICIAL CARBON-14 - A TRACER FOR CARBON IN THE ATMOSPHERE AND BIOSPHERE

THESIS

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SUMMARY

Variations in the steady-state concentrations of natural ^{14}C in the atmosphere, biosphere, and oceans stimulated the application of this isotope as a tracer for the transport of carbon in these various reservoirs, Unfortunately the scope of these early studies was limited by the small differences in the concentrations of natural ^{14}C in the geochemical carbon cycle. In recent years, however, the dispersion of artificial ^{14}C, introduced into the atmosphere during nuclear weapons' tests, has presented a unique opportunity for detailed studies of carbon transport. Further importance was attached to these investigations since artificial ^{14}C constitutes a potential health hazard to mankind.

In this research temporal variations in the distribution of artificial 'bomb' ^{14}C in the atmosphere and biosphere have been studied through analysis of atmospheric CO_2, food chain, and human tissue samples. The data have been used in an examination of the pathways for CO_2 transport in the atmosphere and the rates at which CO_2 is transferred to the biosphere and oceans.

The temporal variations in the concentration of $^{14}CO_2$ in air suggest that diffusion processes are predominant in atmospheric transport, particularly in the/

the stratosphere. The mixing time for $^{14}CO_2$ throughout the atmosphere is comparable with the mean life of a CO_2 molecule in the atmosphere before transfer to the ocean viz., 10 to 15 years.

During the past decade the concentrations of ^{14}C in man have shown significant differences from those in the contemporary atmosphere. This is best explained by the finite times required for the passage of ^{14}C through the food chain and the selective nature of the human diet.

The results of this study suggest that approximately 100 years will pass before the present inventory of artificial ^{14}C becomes uniformly distributed throughout the dynamic carbon cycle. Due to the release of '^{14}C-free' CO_2 by the combustion of fossil fuels (the Suess effect) it seems likely, however, that ^{14}C concentrations in the atmosphere and biosphere will attain pre-bomb levels by the end of this century.

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CHAPTER 1. INTRODUCTION

1.1. General Considerations

The testing of nuclear weapons during the past 25 years has resulted in the pollution of the environment with a wide range of radioactive elements. This artificial radioactivity has increased the radiation dose to which man is normally exposed from natural radioactive elements in the earth's crust and from cosmic radiation. An assessment of the magnitude of this additional radiation dose, both at the present time and in future years, is clearly of prime importance.

During the past 20 years considerable attention has been focussed on the radiation hazard arising from fission product nuclides. Numerous investigations have been reported on factors such as, (i) global fallout patterns, (ii) the passage of fission product nuclides through the food chain, (iii) the deposition of ^{90}Sr and ^{137}Cs in bone, (iv) the potential thyroid damage from ^{131}I, (v) the inhalation dose from short lived nuclides such as ^{89}Sr, ^{95}Zr, ^{106}Ru, ^{140}Ba, and so on. The potentially hazardous character of ^{14}C, although outlined early by Leipunsky [1957], Pauling [1958] and Totter et al. [1958] has not attracted as much attention. Further investigation of this isotope appeared necessary in view of an estimated 95×10^{27} excess ^{14}C atoms (approximately 10 megacuries ^{14}C/

^{14}C) produced to date, and also the enhanced ^{14}C/fission nuclide ratio from thermonuclear devices.

1.2. Nature of the Radiation Hazard

For all artificial radioactivity the potential radiation hazard must be considered from two aspects. First, the availability of the particular nuclide for incorporation into human tissue both at its time of production and in the future. Second, the nature and extent of the biological damage resulting from nuclear disintegrations occurring within the body.

Several factors control radionuclide concentrations in human tissue, viz. the rate of removal of the species from the atmosphere, its mode of entry into the food chain, its significance in human metabolism, and its radioactive decay rate. In many respects the behaviour of ^{14}C is not comparable with that of fission product nuclides. A summary of these basic differences is given in Table 1. Clearly ^{14}C has the most positive access to the food chain, and the radiation dose to the human population must be considered over a far greater time span than the critical fission nuclides.

Biological damage to body tissue is primarily a function of the energy released by the ionizing radiations associated with nuclear disintegration. Thus in the ^{14}C decay process, $^{14}C \longrightarrow {}^{14}N + \beta^- + 0.155$ MeV (max.), damage to/

TABLE 1. Comparison of the Environmental Properties of Fission Nuclides and ^{14}C.

EVENT	FISSION PRODUCTS	^{14}C
Atmospheric processes	Present in aerosol particles. Subject to gravitational settling and washout from the lower atmosphere. Non-uniform global deposition.	Present as gaseous $^{14}CO_2$. Mixes through atmosphere tending towards uniform distribution. Atmospheric concentration diluted by exchange of CO_2 with oceanic carbon.
Entry into the food chain	Deposition on vegetation grazed by domestic animals. Assililation into plant structures (trace quantities). Solution in water supplies.	Via photosynthesis into the basic structure of all plants.
Radioactive decay	Longest lived hazardous nuclides (^{90}Sr and ^{137}Cs) have half lives of 28 years.	Half life 5730 years.

to tissue may arise not only from the ionizing radiation (β^-) but also from the following considerations:

(i) Chemical change from ^{14}C to ^{14}N in organic molecules.

(ii) Recoil energy of the nucleus after beta emission.

(iii) Residual electronic energy within the atom after beta emission.

Damage caused by transmutation from ^{14}C to ^{14}N is particularly significant since carbon is the basic element in the chemical structure of all living molecules. Therefore transmutation alone must be detrimental, particularly where the molecular structure is important to its function. This is the case for those molecules which maintain or replicate the genetic apparatus. Totter et al. [1958] have estimated the mutational consequences of transmutation as being comparable in magnitude to those from the associated ionizing radiation.

From the foregoing discussion it is clear that the total radiation hazard to mankind from artificial ^{14}C must be considered over many generations. Thus the possibility of both somatic and genetic damage must be considered. Measurement of ^{14}C concentrations in contemporary atmospheric, food chain, and human tissue samples will allow an assessment of the radiation hazard to present generations.

generations. Future environmental concentrations of ^{14}C from nuclear weapons tests can only be determined, however, if the transport processes of ^{14}C within the geochemical carbon cycle are fully understood.

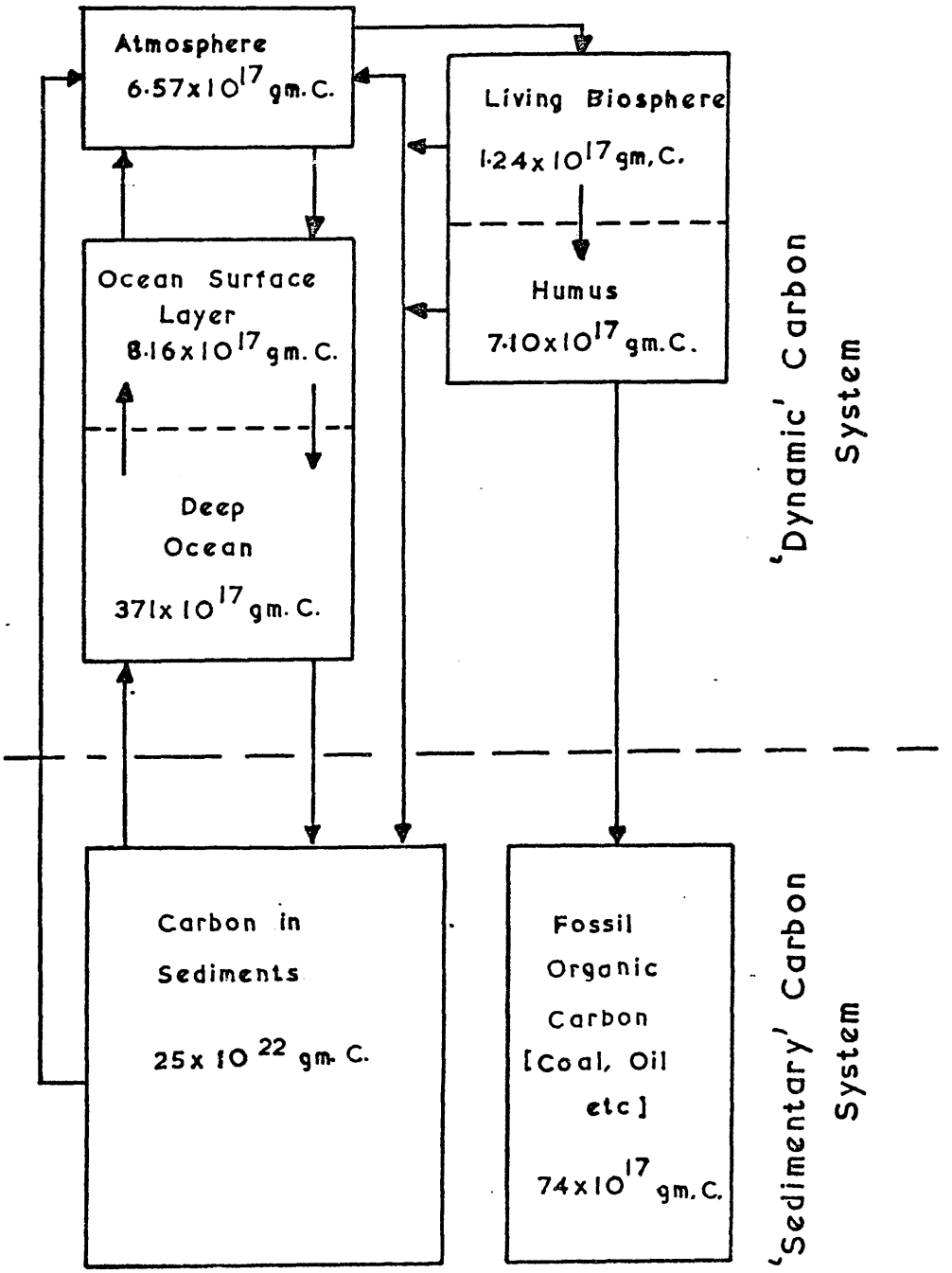
1.3. The Geochemistry of Carbon

(a) The carbon cycle: throughout geological time continuous cycling processes have led to the equilibrium distribution of carbon shown in Fig. 1. The important features of the cycle are the carbon mass distribution and the rates of exchange of carbon among the various reservoirs. These parameters govern the time required for equilibrium to be re-established after any perturbation in the cycle.

Exchange between the 'dynamic' and 'sedimentary' systems takes place very slowly (on a time scale of millions of years). Clearly, therefore, the processes related to environmental considerations are those involved in the 'dynamic' system, since these occur on a time scale of less than a few hundred years.

(b) Carbon isotopes in nature: Three isotopes of carbon are found in nature viz., ^{12}C and ^{13}C, both of which are stable, and the radioactive isotope ^{14}C ($t_{\frac{1}{2}} = 5730 \pm 40$ years [Godwin 1962]). The existence of natural ^{14}C in environmental materials was first predicted/

Figure 1. Distribution of Carbon in the Natural Carbon Cycle



predicted by Libby [1946], and subsequently confirmed experimentally by Anderson et al. [1947].

The isotopic ratio $^{13}C/^{12}C$ in the carbon cycle is approximately 10^{-2} but, due to isotopic fractionation in the transfer of carbon between different chemical phases, slight variations exist in the $^{13}C/^{12}C$ ratios measured for different carbon reservoirs, [Craig 1953]. Thus, for example, the $^{13}C/^{12}C$ ratio of the carbon in plant structures is approximately 1.7% less than that of atmospheric CO_2.

The specific activity of natural ^{14}C in pre-1900 wood has been measured at 14 ± 1 dpm/gm C, [Suess 1955], corresponding to a $^{14}C/^{12}C$ ratio of 1.2×10^{-12}. Isotopic fractionation will also affect the $^{14}C/^{12}C$ ratio in various carboneceous materials. The change for $^{14}C/^{12}C$ being twice that observed for $^{13}C/^{12}C$, [Craig 1954].

(c) Production of natural ^{14}C: Natural ^{14}C results from the interaction of neutrons, produced by cosmic ray events, with nitrogen atoms in the atmosphere. Primary cosmic rays, which are essentially high energy protons, cause nuclear disruption of atoms of the upper atmosphere to produce high energy (approximately 10^3 MeV) neutrons and protons. These neutrons and protons in turn cause evaporation type reactions with the emission of lower energy neutrons (approximately 10 MeV). Atomic interactions further reduce the energy of these secondary neutrons to thermal/

thermal levels (< 2 MeV), and they are subsequently captured by atoms in the atmosphere. The major transmutations are shown in Table 2. Consideration of the cross sections of these reactions and the abundance of nitrogen in the atmosphere, suggest that virtually all of the cosmic ray neutrons contribute to ^{14}C production via the reaction

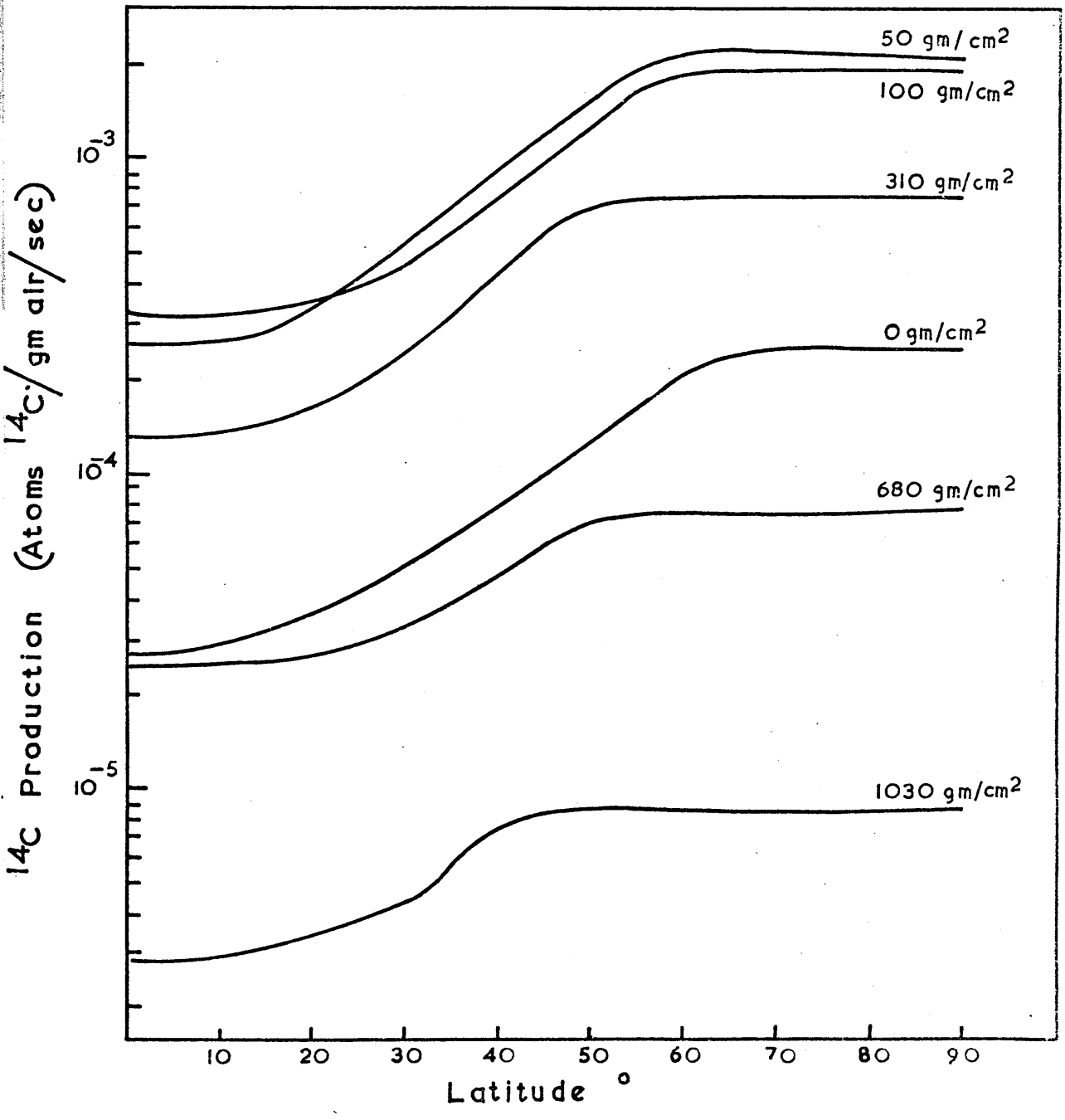
$$^{14}N + n \longrightarrow {}^{14}C + {}^{1}H.$$

The production of natural ^{14}C follows the pattern of the cosmic ray neutron flux incident on the earth and investigations by several workers have shown that this flux is dependent on altitude, latitude, and solar activity. The spatial variation in ^{14}C production as computed by Lingenfelter [1963], from the neutron flux data for a period of minimum solar activity is presented in Fig. 2. A correlation between the neutron flux intensity and the 11 year sunspot cycle has been postulated by Simpson et al. [1953]. These computations suggest that the annual production rate for ^{14}C can vary between $\pm$ 25% with maximum production during periods of minimum solar activity. The existence of a corresponding fluctuation in the $^{14}C/^{12}C$ ratios of recent biospheric materials has been discussed by Baxter [1969]. Cyclic variations in the mean ^{14}C production rate on a longer time scale are also evident. The minimum production rate averaged over the/

TABLE 2. Activation of Atmospheric Atoms by Thermal Neutrons.

REACTION	NEUTRON CROSS-SECTION (Barns)
$^{14}N + n \longrightarrow {}^{14}C + {}^{1}H$	1.75
$^{14}N + n \longrightarrow {}^{11}B + {}^{4}He$	0.2
$^{14}N + n \longrightarrow {}^{12}C + {}^{3}H$	0.01
$^{16}O + n \longrightarrow {}^{17}O + \gamma$	0.02

Figure 2. ^{14}C Production as a Function of Altitude (gm/cm^2), and Geomagnetic Latitude



the earth's surface during the past 10 solar cycles is 2.50 ± 0.50 ^{14}C atoms/cm^2/sec, [Lingenfelter 1963], whereas the most recent estimates of the decay rate are 1.8 ± 0.2 disintegrations/cm^2/sec [Craig 1957], and 1.9 ± 0.2 disintegrations/cm^2/sec [Ferguson 1963]. Thus, despite the large errors involved there is a strong indication that the present natural production rate exceeds the decay rate by as much as 25%. Past inequalities of this magnitude may explain the approximately 200 year oscillations of 1% to 4% measured during dendochronological ^{14}C calibration studies, [Willis et al. 1960, Damon et al. 1966, and Suess 1967].

(d) Distribution of natural ^{14}C: The ^{14}C specific activity in a given reservoir of the carbon cycle is governed by, (i) the rate of exchange, either direct or indirect, with the reservoir of ^{14}C production i.e., the atmosphere, (ii) the fraction of total exchangeable carbon contained in the reservoir, (iii) isotopic fractionation effects, and (iv) the radioactive decay of ^{14}C. Since the cycling time between the 'dynamic' and 'sedimentary' systems is in the region of 4 x 10^5 years [Goldberg et al. 1958], the sedimentary system contains essentially no ^{14}C. An estimate of the natural ^{14}C inventory is given in Table 3. The overall estimate is within ± 5%, but a considerable error possibly a factor of 2, may be involved in defining the relative sizes/

TABLE 3. Distribution of Natural ^{14}C.

CARBON RESERVOIR	INVENTORY (10^{27} ^{14}C atoms)
Atmosphere	37
Biosphere	8
Humus	35
Ocean Surface Layer	45
Deep Ocean	1891
TOTAL	2016

sizes of the biosphere and the ocean surface layer. It is apparent, however, that due to its relatively large size the deep ocean is the dominant reservoir for ^{14}C.

It was reasoned by Libby [1955] that the mean residence time for a ^{14}C atom in any reservoir of the 'dynamic' cycle was short relative to its half-life, so that each atom would complete several passages through the 'dyhamic' cycle during its lifetime. Then, if the ^{14}C production rate and the physical parameters of the cycle had remained essentially constant over the previous 20,000 to 30,000 years a steady state distribution of ^{14}C would be attained. Thus, although the specific activity would vary among the various reservoirs, the value for a given reservoir would be constant with time. These assumptions formed the basis of the ^{14}C dating method. Due to radioactive decay a carbon sample which had ceased to exchange with the 'dynamic' cycle would have a specific activity (A_t), at time t later, equal to

$$A_o \, e^{-\lambda t} \quad ,$$

where A_o is the steady state ^{14}C activity, and λ the disintegration constant for ^{14}C. Thus, for carbon of organic origin 't' is the time elapsed since exchange with the atmosphere viz., death of the organism.

As discussed previously, calibration studies indicate that the steady state concept is not strictly valid. The occurrence and magnitude of the fluctuations in/

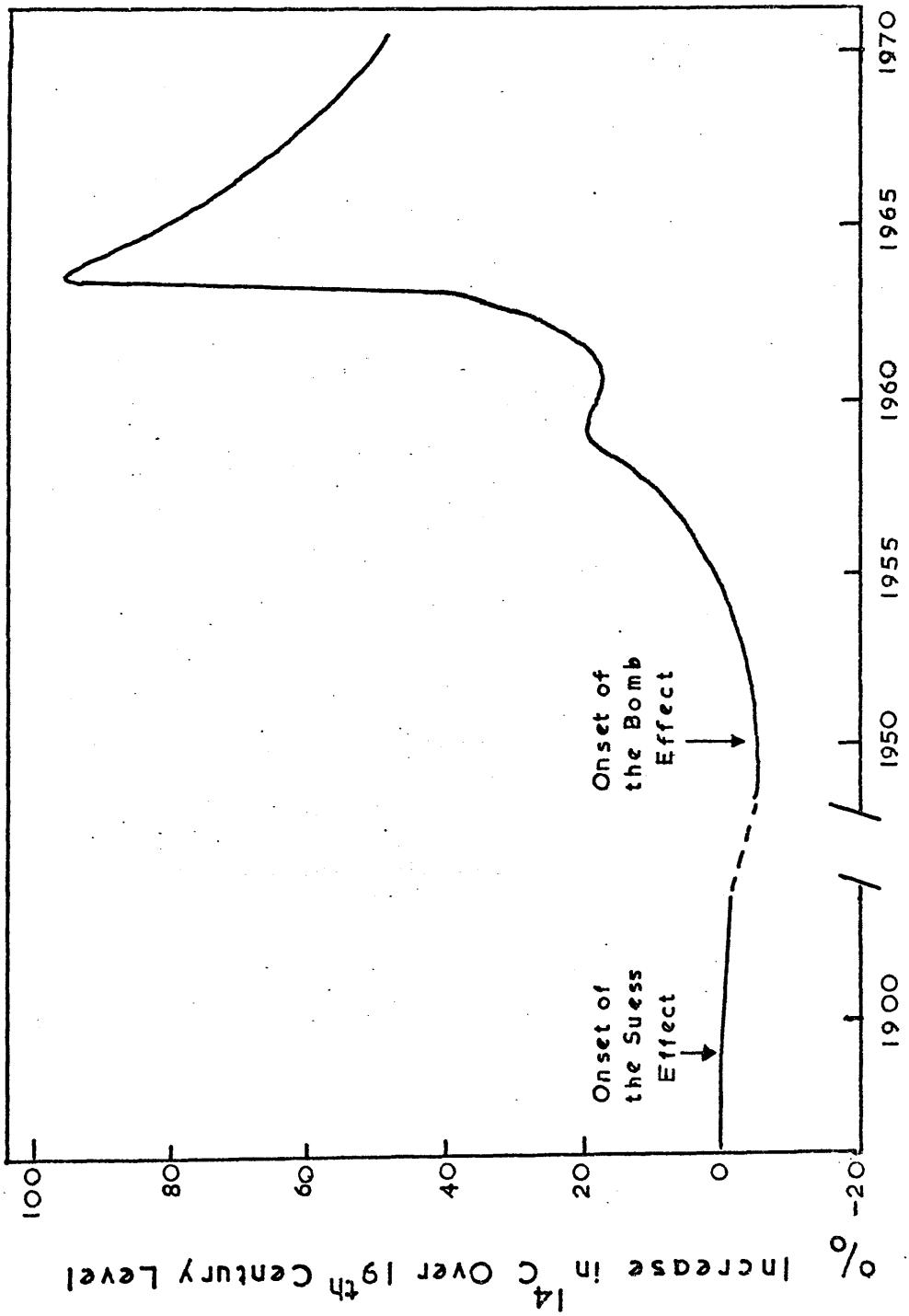
in natural ^{14}C concentrations are extremely significant in ^{14}C chronology. Whereas these natural fluctuations occur over relatively long time periods man has produced significant perturbations during the past century.

1.4. Man Made Changes in the Natural Carbon Cycle

Since the mid 19th century two of man's activities have caused a rapid disruption in the equilibrium conditions of the natural carbon cycle. First, the combustion of fossil fuels has released large quantities of ^{14}C-free CO_2 to the atmosphere, resulting in a decrease of ^{14}C specific activity (Suess effect). Second, the testing of nuclear devices has added ^{14}C to the atmosphere resulting in a corresponding rise in the ^{14}C specific activity (bomb effect). The relative magnitude of these effects as measured in the lower atmosphere of the northern hemisphere, are presented in Fig. 3.

(a) The Suess Effect: This perturbation constitutes a rapid transfer of carbon from the sedimentary to the dynamic system of the carbon cycle. It has resulted in a steady increase in the atmospheric CO_2 content since the onset of the industrial revolution. The total 'fossil CO_2' released until 1950 was estimated by Revelle et al. [1957] as equivalent to 20% of the natural atmospheric content. The corresponding dilution of the specific activity of natural ^{14}C measured in the atmosphere/

Figure. 3. ^{14}C Concentrations in the Lower Atmosphere of the Northern Hemisphere During the Past Century.



atmosphere and biosphere has ranged from 2% to 6% over the past 100 years [Houtermans et al. 1967]. It appears, therefore, that only about 20% of this excess 'fossil CO_2' remained in the atmosphere while the majority was transferred to the hydrosphere. The magnitude of this transfer was confirmed by Broecker [1960] who measured a corresponding decrease of approximately 1% in the steady state ^{14}C specific activity of the ocean surface layer. A recent analysis of the future levels of 'fossil CO_2' contamination [Baxter 1969] shows an increasing significance for this CO_2 source both as a dilutant of environmental ^{14}C activity and as a contributor to possible changes in world climatic conditions.

(b) The bomb effect: ^{14}C produced in the detonation of nuclear devices was first monitored in ground level air during 1954 [Rafter et al. 1957]. Subsequent variations in the atmospheric ^{14}C concentration have been closely monitored by several workers [Tauber 1960, Willis 1960, Nydal 1963, 1965, and 1966, Münnich et al. 1963, Rafter 1965, and Ergin 1969].

^{14}C is produced by the free neutrons that escape during the fission or fusion reactions and are subsequently absorbed by atmospheric nitrogen. As is the case in natural ^{14}C production, it is believed that practically all of these neutrons produce ^{14}C atoms which are then rapidly oxidised to $^{14}CO_2$. The number of ^{14}C atoms

produced/

produced in a nuclear detonation can be calculated if the type of reaction and the energy yield involved are known. In most cases, however, accurate data of this nature are not available and estimates must be made. Some of the reactions utilized in nuclear devices together with the excess neutrons produced per Mton equivalent are listed in Table 4. Apart from the design and energy of the nuclear reaction, ^{14}C production is also dependent on the location of the explosion. A test carried out on the earth's surface produces approximately 50% of the ^{14}C that would result had the same device been detonated high in the atmosphere, since during a 'ground burst' one half of the free neutrons are captured by elements in the earth's crust rather than by atmospheric nitrogen.

The vertical distribution of the ^{14}C produced is a function of the energy, altitude, and latitude of the explosion. Stebbins [1956], has investigated the fraction of the atomic cloud, entraining the $^{14}CO_2$, that enters the stratosphere under varying test conditions (Fig. 4). It is clear that for explosions of 1 Mton and greater essentially all of the ^{14}C produced is injected directly into the stratosphere. This is the case for more than 95% of all the artificial ^{14}C produced to date.

Estimates of ^{14}C production relative to total energy/

TABLE 4. Neutron Production as a Function of Energy Yield for Various Nuclear Reactions

NUCLEAR REACTION	ENERGY RELEASE PER REACTION (MeV)	NEUTRONS PER Mton.
Uranium Fission	180	2.2×10^{26}
$^{3}H + {}^{2}H \rightarrow {}^{4}He + n$	17.6	14.0×10^{26}
$^{6}Li + {}^{2}H \rightarrow 2\,{}^{4}He$	22.4	0
$^{2}H + {}^{2}H \rightarrow {}^{3}H + {}^{1}H$	4.0	Side reactions, therefore strongly dependent on the design of device and the $^{6}Li/^{2}H$ ratio.
$^{2}H + {}^{2}H \rightarrow {}^{3}He + n$	3.2	
$^{6}Li + n \rightarrow {}^{4}He + {}^{3}H$	4.8	
$^{3}H + {}^{2}H \rightarrow {}^{4}He + n$	17.6	

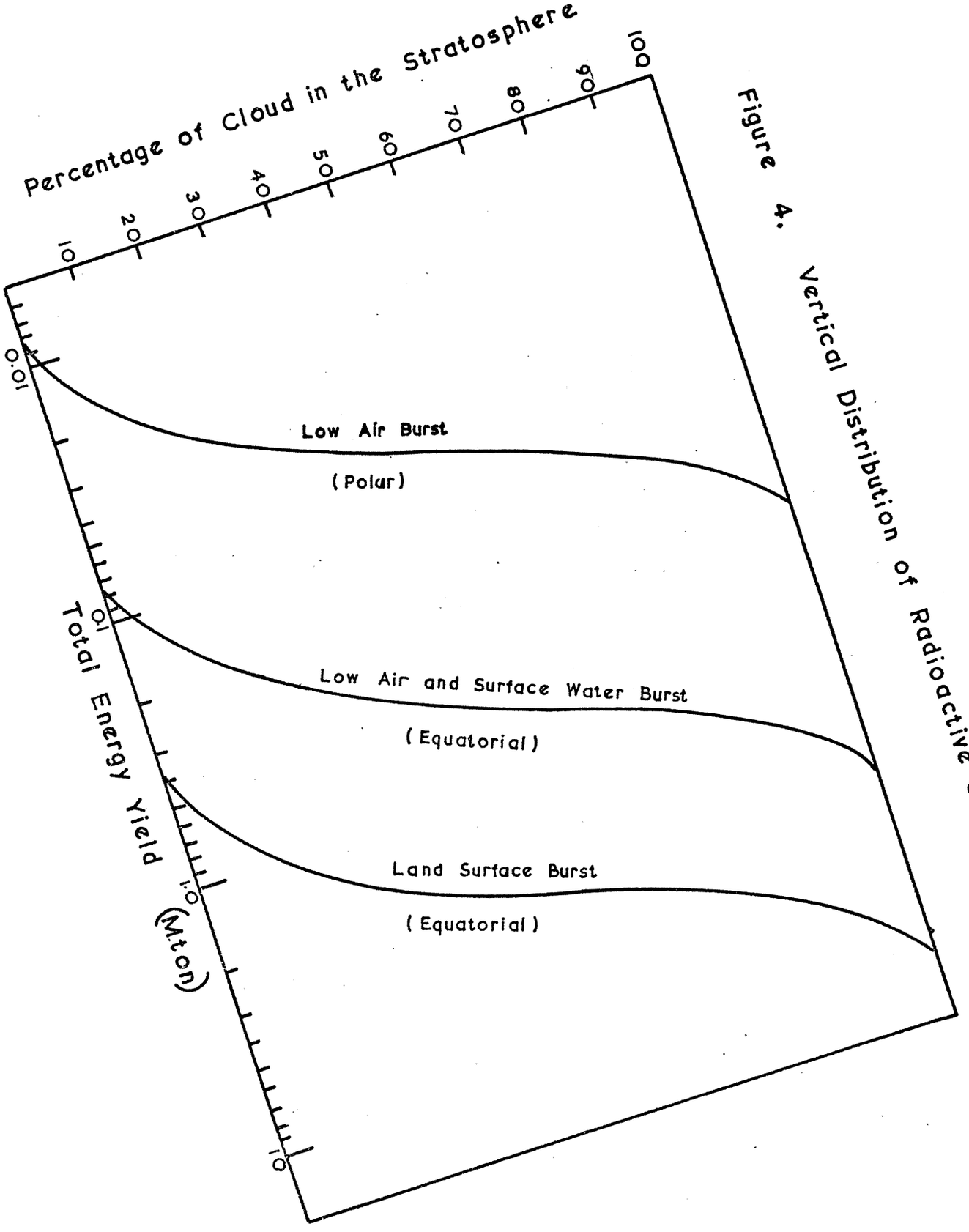


Figure 4. Vertical Distribution of Radioactive Cloud

energy yield have ranged from 4.5×10^{25} atoms/M ton fission [Libby 1956], to 14×10^{26} atoms/Mton fusion [Leipunsky 1957]. The generally accepted values are those proposed by Machta [1959] viz., 2×10^{26} ^{14}C atoms/Mton fission or fusion for an 'air burst', and 1×10^{26} ^{14}C atoms/Mton fission or fusion for a 'ground burst'. The uncertainty in such computations is estimated to be in the region of 100%. The inventory of artificial ^{14}C produced to date, based on the above relationship and published energy yields, is given in Table 5.

Since the error involved in such calculations of the artificial ^{14}C inventory is large, any accurate computation of present and future environmental burden must be based on the direct measurement of excess ^{14}C concentrations in the various reservoirs of the carbon cycle.

1.5. Object and Nature of this Research

To assess the total radiation hazard to mankind from bomb ^{14}C it is necessary to be able to compute and predict the concentration of this isotope in the biosphere at any future date. In due course all of the artificial ^{14}C will be distributed throughout the carbon cycle in much the same manner as natural ^{14}C. Thereafter the magnitude of the radiation hazard will decrease in time relative to the radioactive decay of ^{14}C. Significant transient/

TABLE 5. Estimated 'Bomb ^{14}C' Production to Date.

PERIOD	^{14}C YIELD (10^{27} atoms)
1945 to 1951	0.1
1952 to 1954	6.0
1955 to 1956	3.9
1957 to 1958	14.2
1959 to 1960	nil
1961	24.0
1962	43.4
1963	nil
1964 to 1966	0.02
1967	1.0
1968	2.0
1969	nil
TOTAL	94.62

transient conditions will exist, however, during the next several decades as a result of the finite exchange times between the carbon reservoirs.

In this study contemporary environmental ^{14}C concentrations have been monitored to enable:

(i) A summation of the inventory of artificial ^{14}C produced to date.

(ii) An evaluation of the exchange processes in the natural carbon cycle using bomb ^{14}C as a quantitative tracer.

(a) Conditions for the measurement of carbon exchange

Measurable differences in the ^{14}C specific activities of the various carbon reservoirs permit the application of a mathematical model treatment to mass transport through the dynamic carbon cycle. The construction and evaluation of such box models have been reviewed in detail by Plesset et al. [1960], and many models of varying complexity have been applied to the dynamics of carbon transfer. However, as illustrated in Table 6, considerable uncertainty still exists regarding exchange values. Clearly, the accuracy of the data relating to pre-bomb conditions is limited by the small differences in natural ^{14}C specific activities in the carbon cycle. The production of artificial ^{14}C allows a much more precise assessment of these parameters, and also affords the opportunity to study gaseous transport within/

TABLE 6. Mean Residence Times* (years) of CO_2 in Various Carbon Reservoirs.

AUTHORS	STRATOSPHERE TO TROPOSPHERE	TROPOSPHERE TO OCEAN	BASIS FOR ESTIMATE
Arnold et al. [1957]	-	10 to 20	Natural ^{14}C
Arnold et al. [1957]	-	20	Suess effect
Revelle et al. [1957]	-	10	Suess effect
Craig [1957]	-	7 ± 3	Natural ^{14}C
Fergusson [1957]	-	2 to 10	Suess effect
Rafter et al. [1958]	-	3.3	Bomb ^{14}C
Hagemann et al. [1959]	5	-	Bomb ^{14}C
Broecker et al. [1960]	-	4	Bomb ^{14}C
Junge [1961]	-	2 to 3	Suess effect
Feely et al. [1966]	1.5	-	Bomb ^{14}C
Lal et al. [1966]	0.8 ± 0.3	4	Bomb ^{14}C
Münnich et al. [1967]	-	5.4	Bomb ^{14}C
Bien et al. [1967]		25	Bomb ^{14}C
Nydal [1967]	3.5 ± 0.8	-	Bomb ^{14}C
Young et al. [1968]	1.5	2.5	Bomb ^{14}C
Nydal [1968]	2.0 ± 0.5	5 to 10	Bomb ^{14}C
Walton et al. [1969]	4.0	9.3	Bomb ^{14}C

* The mean residence time is the reciprocal of the exchange rate constant for a given reservoir.

within the atmosphere.

Prior to the 1958 moratorium, nuclear weapons tests had introduced significant quantities of ^{14}C into the atmosphere. By mid 1960 ^{14}C concentrations in the lower atmosphere (troposphere) of the northern hemisphere were approximately 20% above pre-bomb levels. However, the sporadic production of this ^{14}C in both time and space somewhat limited its application as a tracer for atmospheric transport and exchange. The resumption of testing during late 1961 through 1962 was on an unprecedented scale. The large excess of ^{14}C injected into the upper atmosphere during this period could be considered as a new tracer. In addition the bulk of this ^{14}C was produced by a few very large thermonuclear devices exploded by the U.S.S.R. Thus, the ^{14}C production was relatively localised in time and space and more applicable to tracer studies than previous ^{14}C injections. The lack of any significant ^{14}C production in the period 1963 through 1969 presented a unique opportunity to apply this bomb ^{14}C to environmental studies.

(b) Possible sources of error in exchange calculations:

Limitations must be recognised in the application of a model treatment for the assessment of carbon exchange rates/

rates and the subsequent computation of the distribution of artificial ^{14}C with time. No model can represent the true system accurately. Estimates and basic assumptions must be made in model construction and the introduction of bomb ^{14}C as a point source has stressed these limitations which include the following:

(i) <u>The assumption that the transfer of carbon between reservoirs is governed by first order rate constants, and that the internal mixing time for carbon within any reservoir is negligible in relation to these rate constants</u>.

The finite mixing time for ^{14}C in the atmosphere is particularly significant. Measurements of ^{14}C in ground level air collected from a world wide network of sampling stations [Ergin 1969] have shown that uniformity of bomb ^{14}C concentration (to within $\pm$ 5%) was obtained throughout the troposphere only during late 1968. The resistance to mixing is even more pronounced in the stratosphere as has been shown by computations performed during this investigation, and in a recent publication by Telegadas et al. [1969]. Thus in any consideration of stratospheric/tropospheric exchange it must be realised that/

that the mixing and exchange times are of the same magnitude.

(ii) <u>The concept that mass transfer across reservoir boundaries is uniform in location and time.</u>

Atmospheric exchange and mixing patterns show a strong seasonal dependence. Maximum stratospheric/tropospheric exchange occurs at mid latitudes during the spring in each hemisphere. This coincides with the growth period of plants and hence accentuates the transfer of ^{14}C to the biosphere. The non uniform global distribution of the oceans and the dependence of CO_2 exchange across the atmosphere/ocean interface on wind speed [Kanwisher 1963] is also adverse to this assumption.

To date, calculations of the exchange rates between the atmosphere and ocean have assumed an equilibrium mass transfer of CO_2. Due to the Suess effect this reasoning is not strictly valid. The rate of uptake of CO_2 by the oceans is a function of the partial pressure of the gas in the atmosphere. The increasing production of fossil CO_2, therefore, results in a corresponding net transfer of CO_2 from the atmosphere to the oceans. This imbalance in the carbon cycle must be considered in any model/

model treatment particularly in the application of contemporary exchange parameters to future years.

(iii) Uncertainty as to the relative sizes of the biosphere and ocean surface reservoirs.

The uncertainty regarding the mass of biospheric carbon and the diverse physical composition of this reservoir make calculations of a representative value for ^{14}C enrichment rather speculative. Dyck [1965] has likened the biosphere to a rapid pump with a cycling time for atmospheric CO_2 in the region of 25 years. Possible errors in defining the biospheric function are, therefore, significant in establishing contemporary exchange rates via bomb ^{14}C.

Measurements of ^{14}C enrichment in oceanic carbon [Broecker et al. 1960, Bein et al. 1967, Münnich et al. 1967, Nydal 1968, and Rafter 1968] indicate the existence of a 'mixed layer' extending to a depth of approximately 100 meters. Unfortunately the limited number of ^{14}C data available in this region leads to estimates of contemporary ^{14}C concentrations which/

which are probably only accurate to within $\pm$ 50%. The situation is complicated further by the non uniform vertical mixing of this surface water with the very large reservoir of deep water which reputedly has a "radiocarbon age" of approximately 1000 years. However, the corresponding error in tropospheric/oceanic exchange calculations is greatly reduced by the dilution of CO_2 specific activity in the large oceanic reservoirs.

(iv) The assumption that ^{14}C concentrations in man are identical with those of the terrestrial biosphere.

^{14}C concentrations in man will be directly related to the dietary pattern. This favours the assimilation of young terrestrial biospheric carbon and usually includes carbon of marine origin with a lower concentration of ^{14}C.

The metabolic processes which govern the rates of exchange of carbon between various human tissues and the environment must also be considered.

(c) Approach to the problem: For bomb ^{14}C a box model treatment will become more representative of the real system with time. The problem remains, however, in the/

the determination of exchange parameters during the period immediately following bomb ^{14}C production for extrapolation to future years. The changes in ^{14}C specific activities have, therefore, been reviewed over as long a period as possible to investigate and minimise the anomolies arising from localised ^{14}C production.

The ^{14}C concentrations in a variety of atmospheric CO_2, food product, and human tissue samples have been monitored. These data together with values reported by other workers have been employed in an assessment of the present and future levels of ^{14}C in the environment.

Since the access of ^{14}C to mankind is primarily governed by photosynthesis the emphasis of this study has been placed on an evaluation of,

(i) the distribution of ^{14}C in the atmosphere,

(ii) the transport of ^{14}C through the food chain,

and (iii) the occurrence of ^{14}C in human tissue.

A theoretical estimate of the reduction in future biospheric ^{14}C concentrations has been made on the basis of contemporary carbon exchange values and the reduction due to the Suess effect.

CHAPTER 2. EXPERIMENTAL ^{14}C ASSAY

2.1. Introduction

Highly specialized chemical and physical procedures are necessary for the measurement of environmental ^{14}C concentrations. These requirements arise from the low ^{14}C specific activities involved viz., less than 30 dpm/gm C and the weak energy of the beta emission (0.155 MeV max.). To obtain statistically significant data, therefore, the counting arrangement must possess the following capabilities; (i) high beta detection efficiency, (ii) low background, and (iii) stable operating conditions over long periods.

The first successful attempts to monitor natural ^{14}C were performed by Anderson et al. [1947]. An absolute counting efficiency of 5.4% was obtained using a solid carbon source mounted around a windowless Geiger tube, and guarded by massive shielding plus a ring of anti-coincidence counters. The experimental procedures involved in source preparation were laborious, and with the advent of nuclear testing the possibility of source contamination by airborne fission products rendered this technique impractical.

The development of gas counting overcame the problem of contamination and also increased the beta detection efficiency. By using mixtures of CO_2 and CS_2 as a Geiger gas/

gas, Crane [1954] obtained a ^{14}C detection efficiency of 70%. Further improvements in gas preparation and purification techniques allowed the use of CO_2, CH_4, C_2H_2, and C_2H_6 as individual counting gases. These gases could be counted in the proportional region and this fact, coupled with the employment of pulse height analysis, led to a detection efficiency of close to 100% for ^{14}C, [De Vries et al. 1952, Suess 1954, Fergusson 1955, and Olsson 1958].

The application of liquid scintillation counting to ^{14}C measurement was first reported by Hayes et al. [1953]. One of the advantages of this technique is that the total volume of the counting medium is small. Further, the use of massive shielding and anticoincidence circuitry is eliminated since cosmic ray mesons produce large pulses in the scintillator which can be readily accounted for by energy discrimination. Problems remain, however, with dark current 'noise' from the photomultiplier tubes, and difficulties in the quantitative synthesis of benzene from the sample carbon.

Proportional counting of CO_2 was selected for this study. Fergusson [1955] first demonstrated the successful counting of CO_2 and showed that difficulties experienced by earlier workers resulted from the presence of trace quantities/

quantities of electronegative impurities in the counting gas. It was necessary, therefore, to develop a procedure capable of processing large volumes of CO_2 (5 litre atmospheres per sample) to a high degree of purity.

2.2. Atmospheric Sample Collection

A routine programme for the collection of atmospheric samples of CO_2 at ground level, in the upper troposphere, and lower stratosphere began in early 1967.

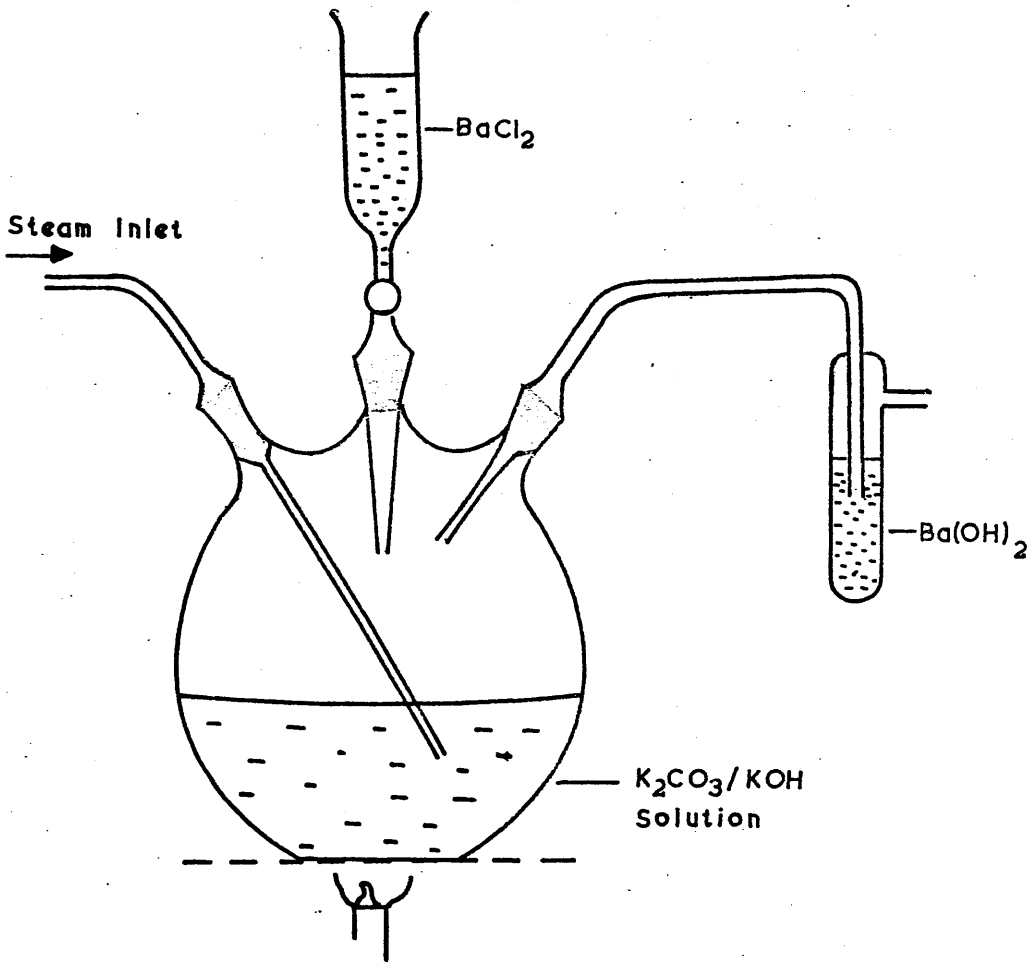
(a) Ground level collection: Initially 3 stations were employed for the collection of ground level CO_2 viz., Chilton [51°31'N. 1°20'W.], Snowdon [53°03'N. 4°0'W.], and Glasgow [55°58'N. 5°0'W.]. It became apparent early in these studies that ^{14}C concentrations monitored at Glasgow were subject to contamination by localized release of large quantities of '^{14}C free' CO_2. Consequently the sampling at this station was discontinued.

A static collection technique was employed to obtain cumulative monthly collections of CO_2 from each station. Aliquots of 250 ml. 8M KOH solution containing 5 gm/litre Ba^{2+} ions were exposed to the atmosphere in basins of surface area approximately 100 cm^2. The basins were exposed under a canopy to avoid dilution by precipitation. A concentration of 8M KOH was chosen from considerations of the rate of CO_2 absorption as a function of ionic strength, the mass of carbon required for ^{14}C assay, and the/

and the problems involved in the handling and storage of caustic solutions. Ba^{2+} ions were included to ensure that any 'contaminant' CO_2 absorbed prior to exposure was precipitated as $BaCO_3$ in the bulk storage container, and subsequently avoided by decantation into the exposure basins. All bulk KOH was prepared at Glasgow University and forwarded to the collectors. $BaCO_3$ which precipitated during exposure was included in the samples returned to Glasgow, and the basins were washed between exposures to avoid memory effects.

In the laboratory the absorbed CO_2 was converted to $BaCO_3$ to allow both convenient storage, and measurement of the collection yield. The carbonate was precipitated by the addition of saturated $BaCl_2$ solution to the KOH/K_2CO_3 solution. To avoid absorption of CO_2 from the laboratory atmosphere the reaction was carried out in a closed system (Fig. 5). Steam, produced from 'CO_2 free' water, was passed through the basic solution and the $BaCl_2$ added via a dropping funnel. The contents of the reaction vessel were allowed to boil for approximately 15 minutes to coagulate and digest the precipitate. The carbonate suspension was then filtered, washed free of Cl^- and OH^-, dried, weighed, and stored in sealed jars. Trial runs, during which '^{14}C free' CO_2 was absorbed and recovered, showed no measurable/

Figure 5. Precipitation of $BaCO_3$ From Ground Level Collections



measurable atmospheric contamination during this procedure.

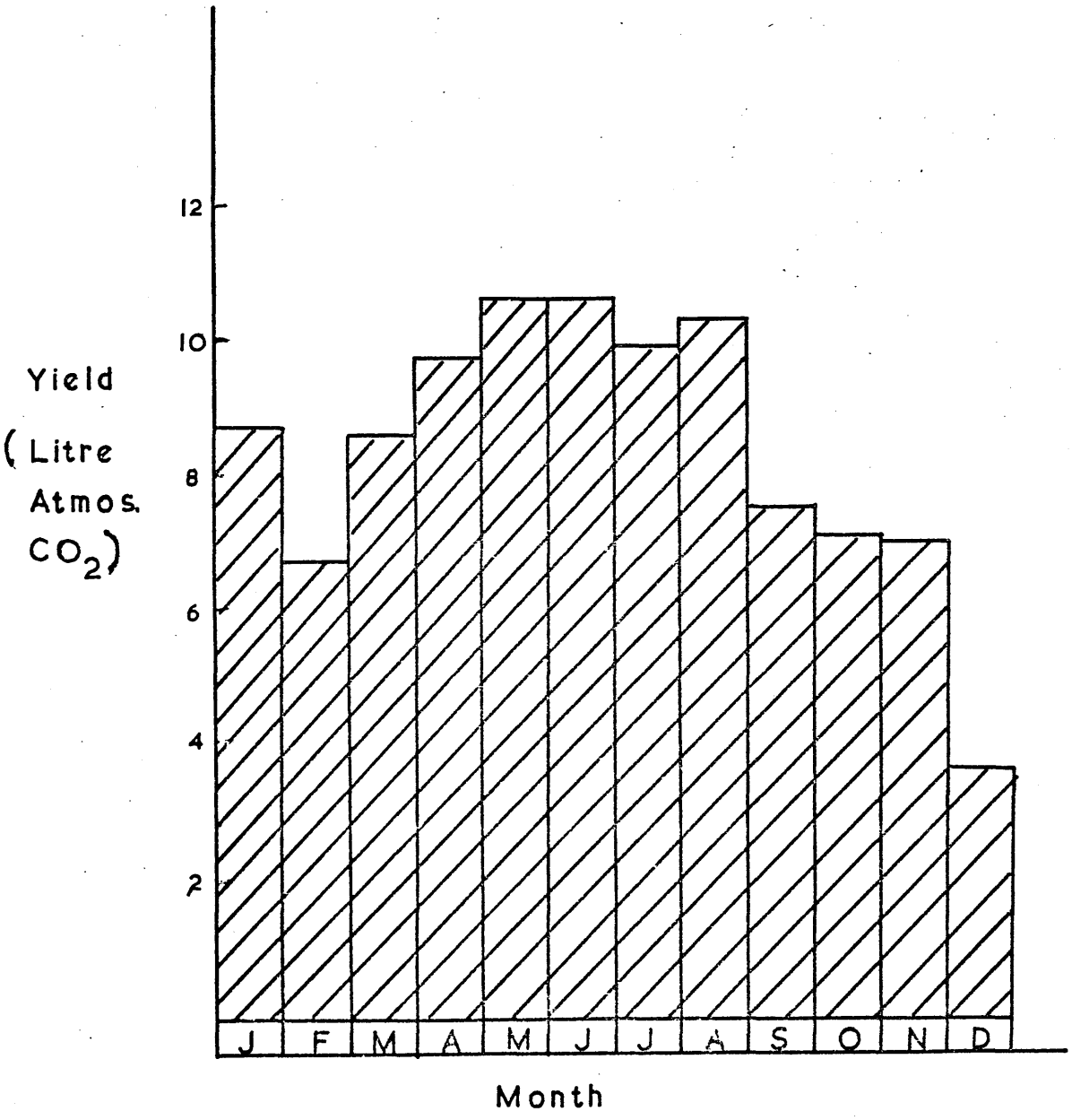
A seasonal variation in CO_2 collection efficiency was evident at both stations (Fig. 6). It was assumed that these variations were a function of the seasonal differences in air temperature.

(b) Altitude collection: Samples of CO_2 from the upper atmosphere were collected in collaboration with The Central Reconnaissance Establishment, R.A.F. Brampton.

Methods available for the collection of litre quantities of CO_2 are severely limited by the low temperature and low pressure conditions prevailing at altitudes around and above the tropopause region. The suitability of Linde Molecular Sieve Type 4A for quantitative adsorption of CO_2 under these adverse conditions was first demonstrated by Fergusson [1963]. Successful applications of this adsorbent have since been reported by Godwin et al. [1964], and Gudiksen [1967]. Alternative methods involve the collection of air either in large containers flown on balloons (Hagemann et al. 1959], or from aircarft by compression into high pressure cylinders [Hagemann et al. 1965].

The collection procedure used in this study was based on the aircraft sampling technique developed by Willis [1966].

Figure 6. Seasonal Variation in CO_2 Collection Yield



Type 4A molecular sieve, in the form of 1/8 inch diameter pellets, was contained in copper mesh baskets, each basket being charged with 500 gm sieve. Immediately prior to take-off 4 baskets were loaded concentrically into each of 2 cylindrical ducts mounted on the wings of the aircraft. The ducts were sealed by retractable rubber bungs controlled from within the aircraft, and each duct operated independently. Thus, for any flight 2 sample collections were possible. In most cases the flight pattern was designed to allow collections at approximately 2000 ft. above and below the tropopause. During the sampling period the sealing bungs were retracted thus exposing the sieve baskets to airflow through the duct. Under normal conditions a 20 minute exposure was adequate for the collection of approximately 4 litre atmospheres CO_2. Immediately after each flight the sampling apparatus was unloaded, sealed in plastic envelopes, and returned to the laboratory. A copy of the flight log containing relevant meteorological data was included with the samples.

In the laboratory the sieve was weighed to determine the amount of atmospheric water adsorbed and then processed to/

to recover the CO_2. Since the reported methods for CO_2 recovery and sieve regeneration proved lengthy an alternative technique was developed in which these processes were carried out independently. CO_2 adsorbed on the sieve was displaced by water vapour and precipitated as $BaCO_3$ in basic solution. Desorbed sieve was cleaned for reuse by drying, first in air and finally in a vacuum oven.

Malfunction of the duct sealing system during some flights resulted in a loss of CO_2 due to the preferential adsorption of atmospheric moisture. Regions of high humidity were avoided during the 20 minute sampling periods, but passage through dense cloud could occur, on occasions, during the remainder of the flight. Therefore, samples which recorded a high water content were regarded as invalid due to possible duct leakage.

2.3. Biospheric Sample Collection.

The isolation of particular carbon fractions from the biospheric samples studied in this research was carried out by various chemical pretreatment procedures. The separated fractions were then converted to CO_2 in a combustion train and the gas collected by precipitation as carbonate in basic solution.

(a) Sample pretreatment: The degree of chemical pretreatment/

pretreatment was dependent on the particular sample.

(i) Milk samples were supplied in powdered form and required no pretreatment.

(ii) Vegetable, meat, fish muscle, and plankton samples were washed in distilled water, finely divided, and dried.

(iii) Samples of human soft tissue were masticated to a puree in distilled water and the suspension freeze-dried,

(iv) Bone samples were separated into mineral, protein, and marrow fat fractions. The bone was split into fragments of approximately 1 cm maximum dimension then boiled in 2M NH_4OH to release the fat into the aqueous phase. The fat was separated by benzene extraction and finally recovered from the solvent by distillation. The solid material was washed, transferred to a sealed system, and digested in 2M HCℓ. CO_2 evolved from hydrolysis of the mineral carbonate was collected in a series of wash traps charged with $KOH/Ba(OH)_2$ solution. Hydrolysis of the protein (collagen) fraction to/

to its constituent α-amino acids occurred during the digestion and these remained dissolved in the bulk solution. This organic fraction was recovered, adsorbed on the mineral [$Ca_3 (PO_4)_2$] residues by evaporation of the bulk solution to dryness.

(v) Blood plasma samples were obtained in a predried form to which small, but known, quantities of dextrose and sodium hydrogen citrate had been added. Since these additives constituted carbon contamination the following treatment was employed to isolate the blood protein fraction. The plasma was reconstituted in distilled water and the total protein fraction precipitated by the addition of 50% w/v trichloroacetic acid solution. The protein was recovered by filtration then washed free from dextrose, citrate and acetate using 2M HCℓ followed by water. Better than 90% recovery of pure protein was obtained using this procedure.

To investigate possible contamination by acetate radicals included in the recovered protein, fractions were separated from the same plasma sample via the technique described and/

and alternatively using $(NH_4)_2\ SO_4$ as precipitant. Comparison of the measured ^{14}C activities of these fractions (Table 7) showed agreement within the limits of counting error (2σ). Thus, the degree of contamination from the chemical reagents was regarded as negligible.

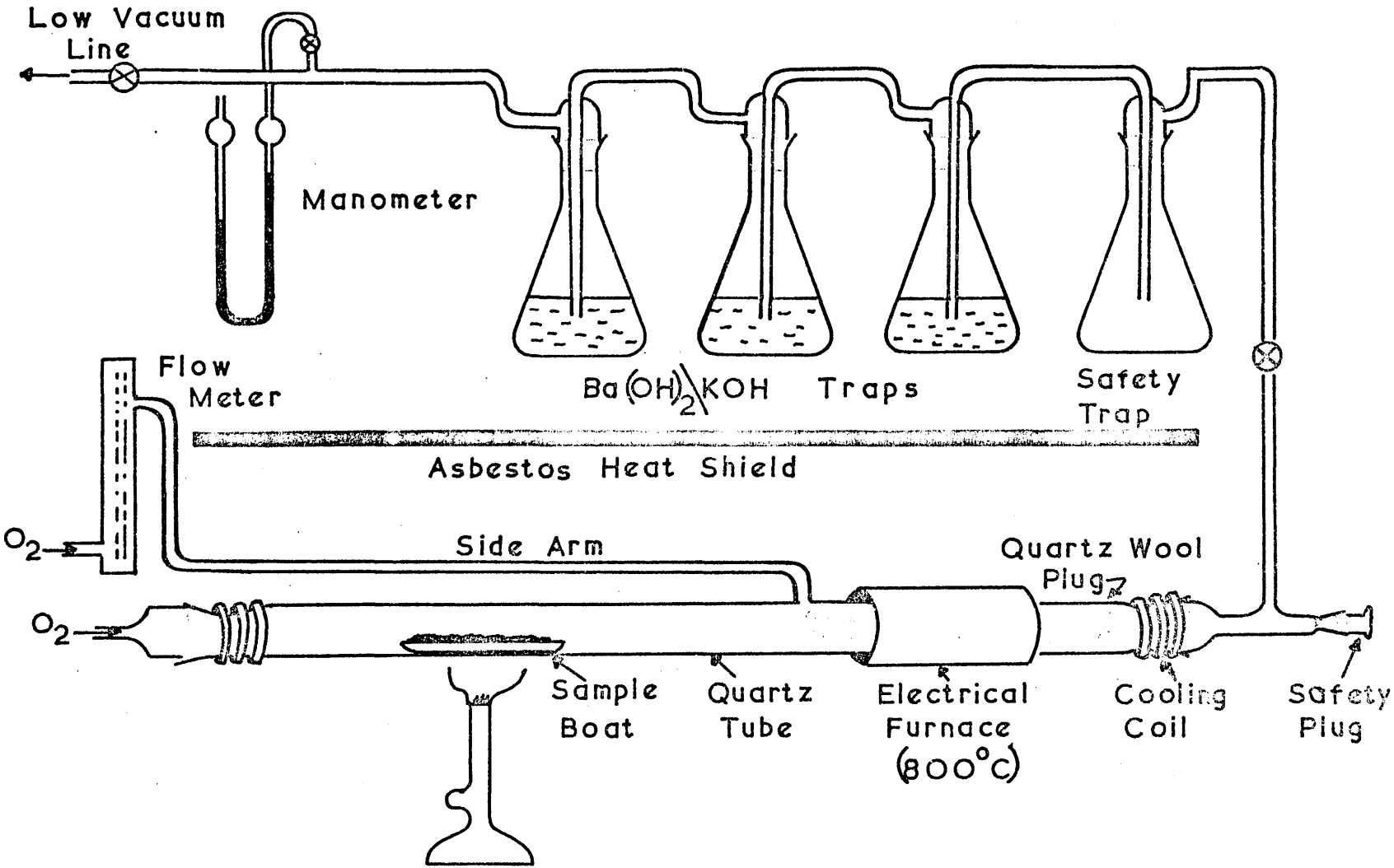
(b) Sample combustion: All organic fractions were oxidised to CO_2 in a stream of O_2. The CO_2 was collected as $BaCO_3$ by absorption in $KOH/Ba(OH)_2$ solution (Fig. 7).

Attempts were made initially to utilise a combustion and collection system similar to that reported by Rafter [1965] in which the CO_2 was cleaned by chemical scrubbing in wash towers and finally collected as "dry ice" suitable for final purification. This technique proved unsatisfactory due to the large quantities of chlorine and nitrogen compounds present in the combustion gases. These impurities quickly exhausted the wash solutions and contaminated the "dry ice" leading to difficulties during the final purification stages. Further, the chemical combination of $C\ell_2$ with the CuO produced a fused mass which caused blockage and eventual rupture of the quartz combustion tube. The furnace section was therefore retained in the system but the CuO was replaced by a plug of quartz wool. The secondary O_2 flow through the side arm was adequate/

TABLE 7. Comparison of ^{14}C in Blood Protein Separations.

PLASMA SERIAL NO.	BLOOD COLLECTION DATE	PROTEIN PRECIPITANT	^{14}C CONCENTRATION $\Delta\% \pm 1\sigma$
EP.142	26.11.52	CCl_3COOH/HCl	-2.9 ± 0.6
"	"	$(NH_4)_2 SO_4$	-3.1 ± 0.5
EP.1315	23. 4.55	CCl_3COOH/HCl	-1.3 ± 0.5
"	"	$(NH_4)_2SO_4$	$+0.1 \pm 0.6$
IRP.60.2212A	23. 6.61	CCl_3COOH/HCl	16.9 ± 1.0
"	"	$(NH_4)_2SO_4$	17.3 ± 0.8
RP67.1476B	8. 5.67	Cl_3COOH/HCl	65.3 ± 0.7
"	"	$(NH_4)_2SO_4$	65.2 ± 0.7

Figure 7. Combustion and CO_2 Collection Train.



adequate to ensure complete oxidation of the sample carbon.

Where possible sufficient material was combusted to yield approximately 5 litre atmospheres CO_2. Each absorption trap for evolved CO_2 was charged with 100 ml. 4M KOH and 20 gm $Ba(OH)_2$. Precautions, as outlined previously, were taken to avoid atmospheric contamination in the preparation of these absorption traps. The flow of O_2 through the side arm was constant at 150 ml/minute, whereas the flow rate through the main tube was varied to control the rate of combustion. A negative pressure gradient of about 10 cm Hg was maintained throughout the system by pumping at the outlet. The pressure gradient was controlled by the valve and monitored with the mercury manometer. The sample combustion rate was kept to a minimum to avoid incomplete oxidation and possible isotopic fractionation of carbon. A small degree of fractionation may, however, have occurred during the combustion but this was compensated through mass spectrometric measurement of the $^{13}C/^{12}C$ ration in the final counting gas.

2.4. CO_2 Production and Purification.

Successful proportional counting of CO_2 is highly dependent on extreme gas purity. Electron (beta particle) loss due to collection by electronegative impurities in the counting gas must be kept to a minimum. Fergusson [1955]/

[1955] has estimated that this loss must be less than 1% which corresponds to tolerance levels of 1 ppm O_2 and 0.1 ppm Cl_2. Additional contaminant species which must be avoided include fluorine compounds and oxides of sulphur and nitrogen.

The problems involved in routine processing of relatively large volumes of CO_2 (approximately 5 litre atmospheres) within such limits demanded an exacting technique. A vacuum gas handling system (Fig. 8) constructed in Pyrex was used. Vacuum conditions were maintained by two manifold systems which could be independently connected to any section of the system. High vacua (10^{-4} Torr) were provided by a Hg diffusion pump backed by a 2 stage rotary pump. The low vacuum manifold was fitted with a single stage rotary pump, and used to produce coarse vacua (10^{-2} Torr) when required viz., during combustion or hydrolysis reactions.

The purification procedure, as outlined in Fig. 9, is a modified version of those reported by De Vries et al. [1953] and Rafter [1965]. The initial stage in purification was the precipitation of all sample carbon as $BaCO_3$. CO_2 was released from the $BaCO_3$ by acid hydrolysis (H_3PO_4 50%) under reduced pressure (Fig. 10). The CO_2 gas was collected in a liquid N_2 cooled finger, isolated/

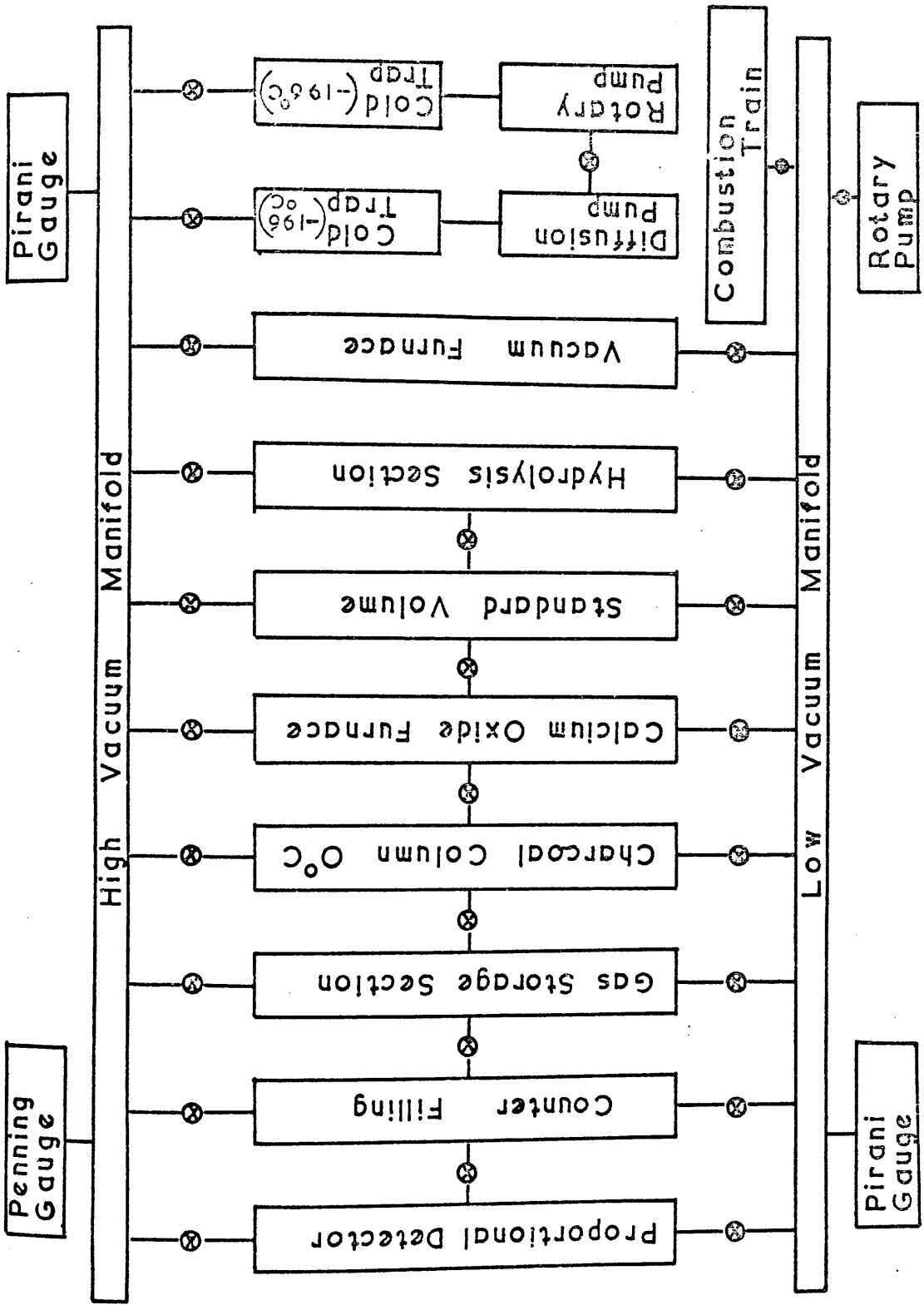


Figure 8. Vacuum Gas Handling System (Diagramatic).

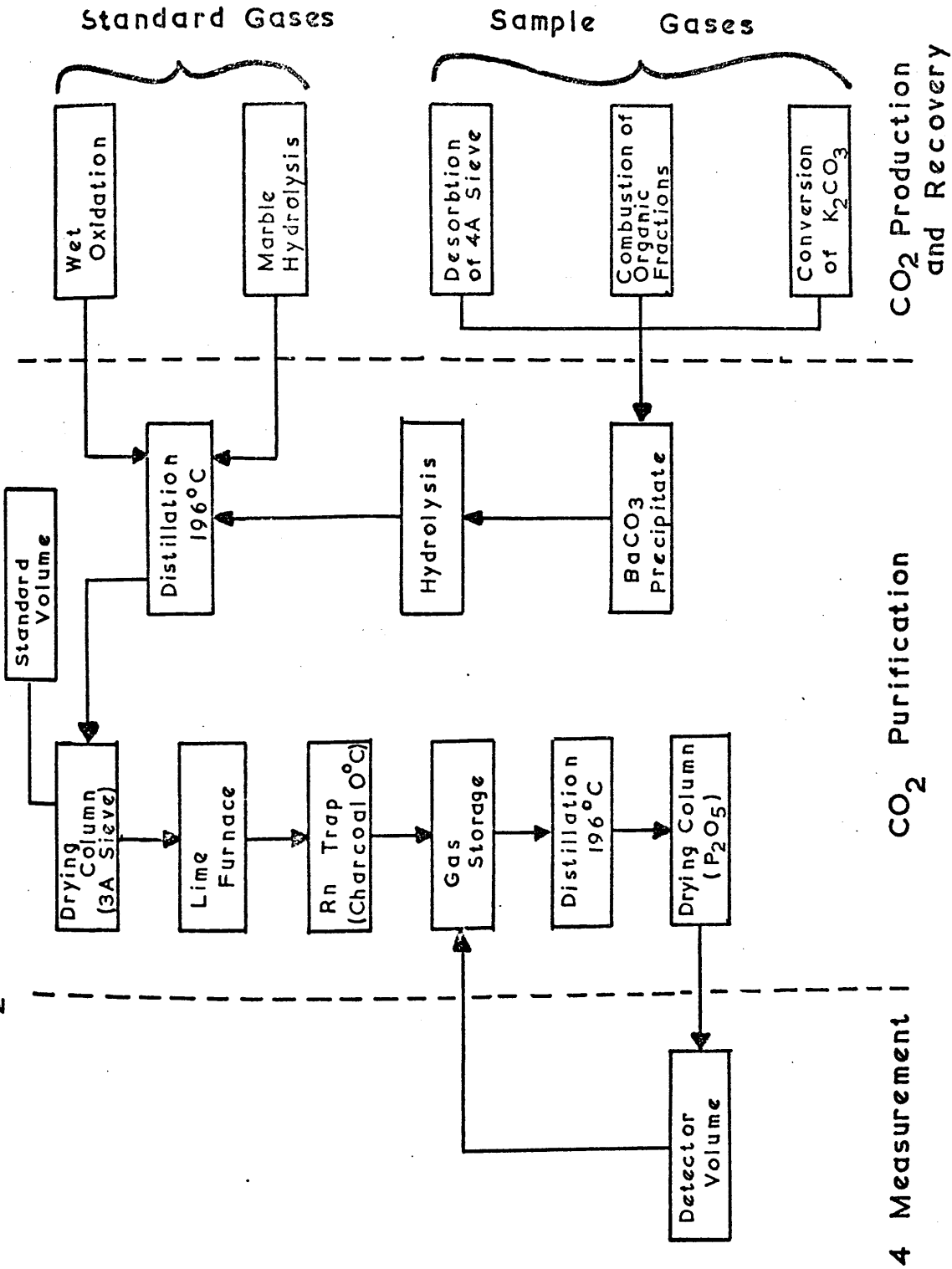
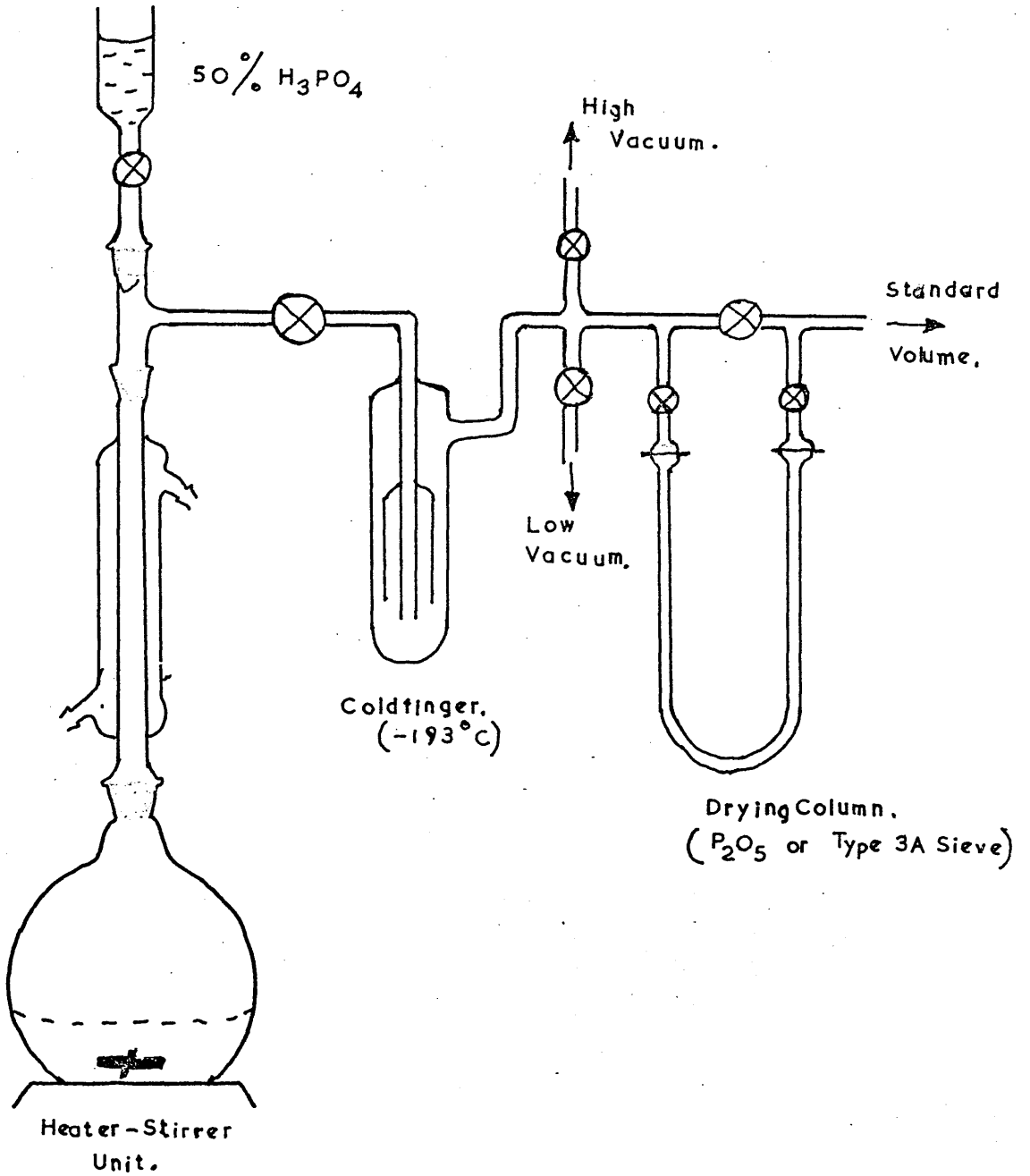


Figure 9. CO_2 Purification Procedure

Figure 10. Hydrolysis and Gas Drying System.



and pumped to 10^{-2} Torr. The CO_2 was then allowed to sublime and pass through a drying column of P_2O_5 into the high vacuum section of the system. At this stage the gas was expanded into a calibrated volume and the yield measured.

The main purification treatment was based on the reaction,

$$Ca\ O + CO_2 \rightleftharpoons CaCO_3.$$

The heat of dissociation of $CaCO_3$ is such that the equilibrium pressure of CO_2 over the reaction is extremely temperature sensitive (Fig. 11). Thus $CaCO_3$ produced from sample CO_2 is stable to high vacuum conditions (10^{-3} Torr) at temperatures below 400°C. The CO_2 is readily recovered by dissociation of the $CaCO_3$ at higher temperatures.

CO_2 in the standard volume was condensed into a cold finger (-196°C), pumped to 10^{-3} Torr, then expanded onto 60 gm CaO contained in a quartz tube at a temperature of 700°C (Fig. 12). The temperature of the system was then lowered to 350°C and volatile impurities removed by pumping the $CaCO_3$ to 10^{-3} Torr. The furnace temperature was then raised to 850°C and the 'pure' CO_2 evolved was distilled into a liquid N_2 cooled finger.

Non volatile impurities on the lime are not released at/

Figure 11. Partial Pressure of CO_2 Over The Reaction $CaO + CO_2 \rightleftharpoons CaCO_3$ as a Function of Temperature.

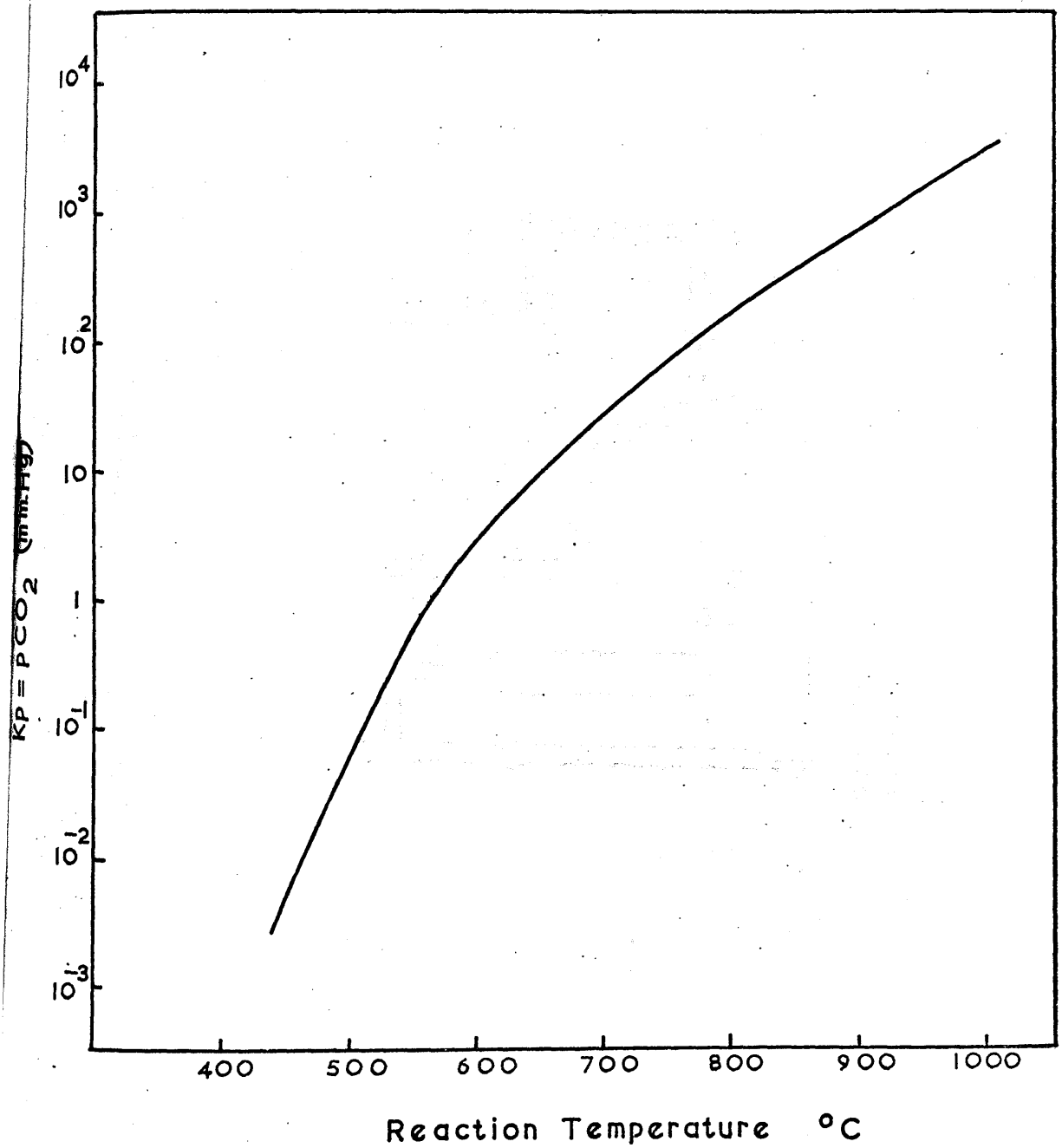
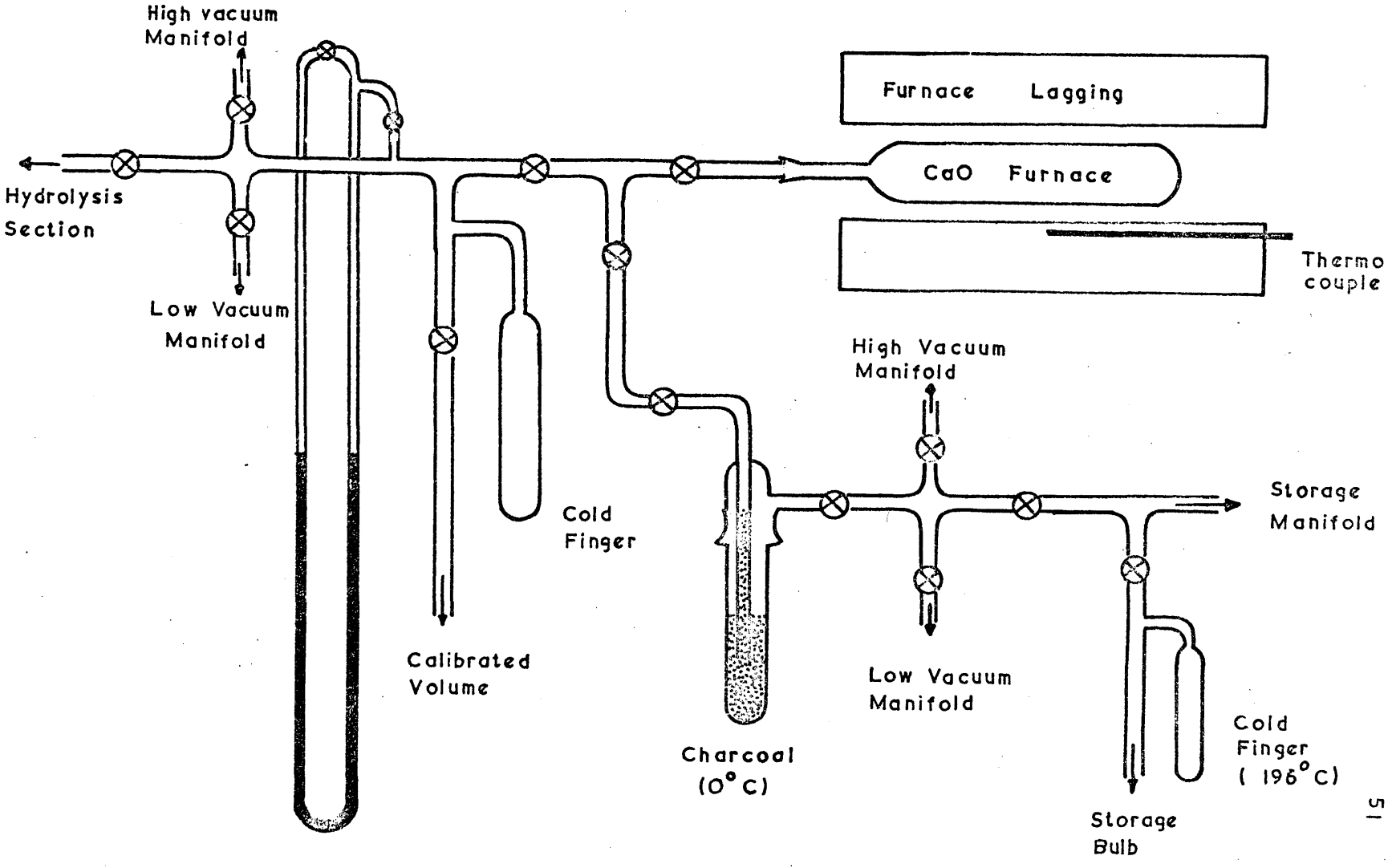


Figure 12. CaO Furnace and Radon Reduction System.



at temperatures below 1000°C [De Vries 1953]. After each CO_2 purification cycle the lime was cleaned by raising the temperature to 1100°C and pumping to 10^{-3} Torr.

CO_2 released from the furnace contained traces of Rn arising from Th and U impurities on the lime. Since ^{222}Rn is an alpha emitter with beta active daughters its presence contributed to the sample activity. To reduce the Rn content the CO_2 was passed through a column of activated charcoal held at 0°C.

The CO_2 was finally collected in a liquid N_2 cooled finger (-196°C), distilled to a residual pressure of 3×10^{-4} Torr, and then expanded into a 5 litre glass bulb. A minimum period of 12 days was allowed between purification and counting to ensure decay of the last traces of ^{222}Rn ($t_{\frac{1}{2}}$ = 3.8 days) and its daughter products.

(a) Background Gas - CO_2 Production: Sources used in the production of non-active CO_2 were anthracite, marble, and commercial 'dry-ice'.

Anthracite was boiled in 2M HCl, washed with distilled water, dried, and then combusted in a stream of O_2. The CO_2 was collected as $BaCO_3$ and subsequently recovered as 'dry-ice' after hydrolysis with 50% H_3PO_4.

Marble/

Marble chips were treated with 2M HCℓ to remove the outer 25% by weight, washed in distilled water, and dried. Two procedures were then used for the production of CO_2. The chips were either hydrolysed with 50% H_3PO_4 and the CO_2 collected as 'dry-ice' or alternatively the chips were loaded into the quartz furnace, pumped to 10^{-3} Torr at 400°C, and the CO_2 recovered through dissociation of the $CaCO_3$ at 800°C.

Commercial 'dry-ice' was simply sublimed under vacuum and distilled into a cold finger at -196°C.

All CO_2 samples collected in the above procedures were purified and stored as previously described.

Intercomparison of the counting rates of CO_2 produced from these various materials showed agreement within $\pm 2\sigma$ counting error. Since the sources of carbon, and the methods of CO_2 production were diverse the measured background data were assumed free from ^{14}C activity.

(b) Modern standard gas - CO_2 Production: Modern standard CO_2 was prepared from the National Bureau of Standards Oxalic Acid Standard through a wet-oxidation technique.

Saturated $KMnO_4$ solution was added dropwise to the/

the oxalic acid in 0.5 M H_2SO_4 solution until the oxidation reaction was complete. The CO_2 was then purified and stored as previously described.

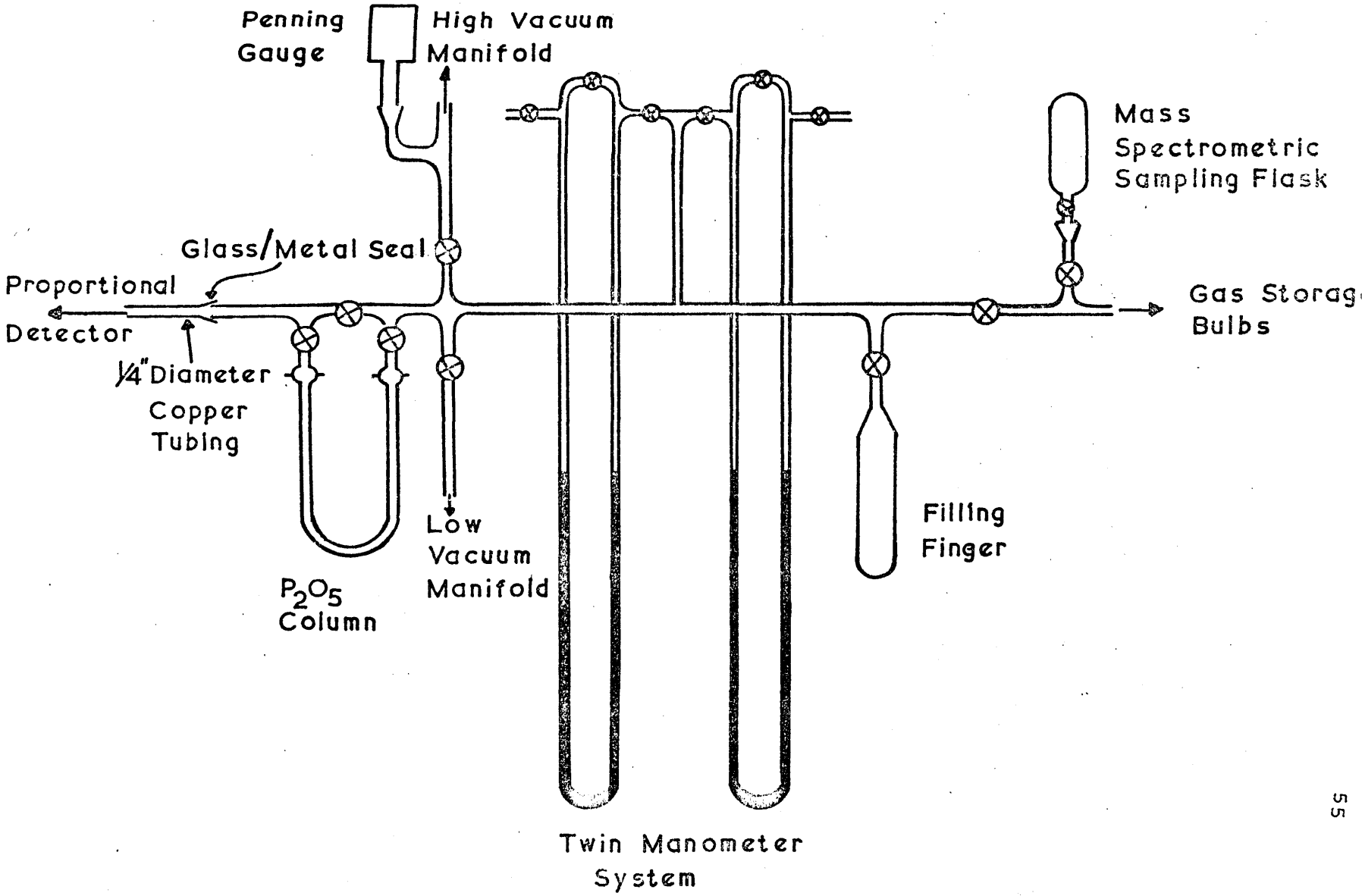
Care was taken to ensure that reaction was carried to completion to avoid isotopic fractionation.

(c) Counter filling: The gas filling system was connected to the detector volume by $\frac{1}{4}$ inch diameter O.F.H.C. copper tubing (Fig. 13). Valves which contained teflon surfaces were avoided in this section due to the possibility of fluorine contamination.

Prior to filling, the combined detector and filling system were pumped to 5×10^{-4} Torr. CO_2 was then transferred from its storage bulb, frozen into the liquid N_2 cooled filling finger, and distilled to 3×10^{-4} Torr at -196°C. The CO_2 was then allowed to sublime and expand into the detector volume via a U-tube drying column packed with P_2O_5.

Filling pressures up to 2 atmospheres were monitored on a twin manometer unit and the temperature inside the counter shield recorded with a gas thermometer. To ensure a constant mass of CO_2 within the detector the pressure of each gas fill was adjusted to correspond to a specific temperature (under routine conditions 760 mm Hg at 15°C). A period of 10 to 15 minutes was allowed for the gas temperature to reach equilibrium with its surroundings before the final pressure adjustment was made.

Figure 13. Counter Filling System.



After a counting sequence the CO_2 was transferred directly to its storage bulb. When ^{14}C measurement was complete a small sample of the CO_2 was retained for subsequent $^{13}C/^{12}C$ analysis.

(d) Measurement of Isotopic Fractionation:

Fractionation occurs in the transfer of carbon between different phases of the environment [Craig 1953]. It is also liable to occur during the collection, production, and purification of CO_2. A correction for this effect is, therefore, necessary before measured ^{14}C concentrations are directly comparable with a specified standard activity.

The degree of fractionation in each sample gas was measured by comparing its $^{13}C/^{12}C$ ratio with that of the primary P.D.B. Chicago Limestone Standard. ^{13}C enrichment values relative to the standard are quoted according to Craig [1961]:

$$\delta^{13}C = 1000 \left[\left(^{Rs}/Rp\right) - 1 \right] {}^{o}/oo$$

where $Rs = {}^{13}C/{}^{12}C$ in the sample,

and $Rp = {}^{13}C/{}^{12}C$ in the standard.

Measurements of $\delta^{13}C$ to an accuracy of $\pm$ 1°/oo ($\pm 2\sigma$) were made using the M.S.3. mass spectrometer at the National Physical Laboratory, Teddington.

2.5. Gas Counting System

^{14}C measurement was based on a Johnstone Laboratories Beta/

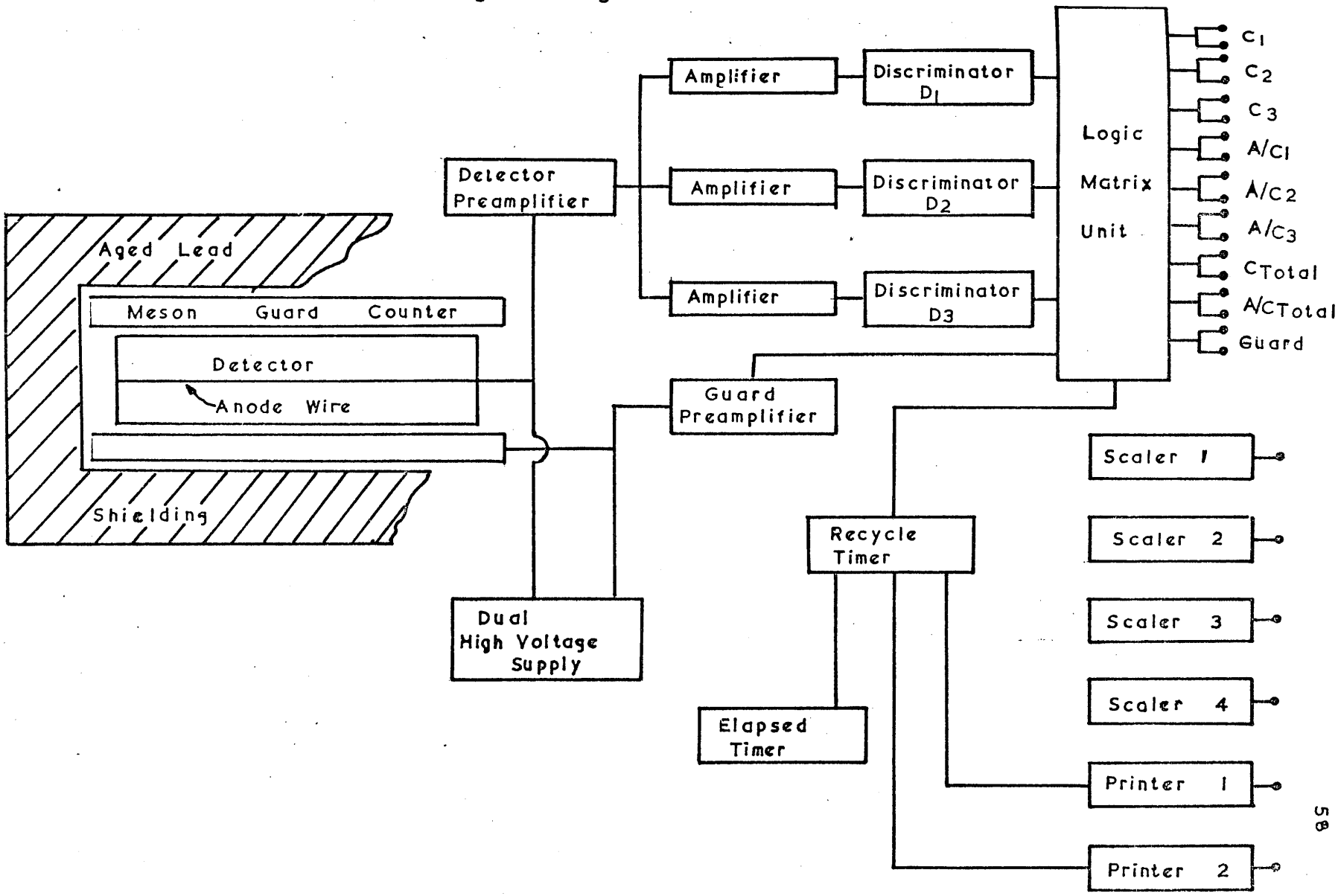
Beta Logic Gas Counting System (Fig. 14).

(a) Detector and guard assembly: The 2.6 litre proportional detector was constructed from heavy wall O.F.H.C. copper tubing and was fitted with a 1 mil stainless steel anode wire. It was housed inside an annular multi-anode guard detector which was operated as a flow Geiger counter using Q-gas (98.7% He,, 1.3% isobutane). The two counters were enclosed in a 4 inch thick 'aged lead' shield to reduce the background from external sources. Pulses registered in both counters were fed via charge sensitive preamplifier units to an electronic console.

(b) Electronic console: Pulses from the pre-amplifier were shaped by a 20 microsecond time constant and fed to a series of 3 variable amplifier - discriminator units. These units sorted the pulses into energy channels which were preset for optimum ^{14}C measurement. The pulses were then transferred to a diode matrix logic unit for time-coincidence analysis with the meson guard pulses. The logic unit utilized the total pulse spectrum to provide 3 energy channel outputs both in coincidence and anti-coincidence with the guard counter. It also supplied total coincidence, anticoincidence, and meson guard signals.

Four scalers, each consisting of a cold cathode decade followed by a 5 digit register, and 2 automatic data/

Figure 14. ^{14}C Counting Arrangement.



printers were available for data monitoring. The cycle time of the printing scalers was determined by an automatic reset-timer control, and thus these printers could be used to monitor non-statistical variations in any chosen output during a counting sequence.

(c) E.H.T. Supply: The console also housed a transistorized dual high voltage power supply for detector and guard operation. The guard supply had a range of 0.5 to 4.1 KV, and the detector supply a range of 0.5 to 6.1 KV. Minimum adjustment for both ranges was 1 volt.

2.6. Counter Operation

(a) Energy discrimination: The proportional detector was operated at a constant gas gain of approximately 5×10^3. A 20 pF capacitor was used in the preamplifier to integrate the anode signal. Since the relationship between beta particle energy (E KeV) and the output signal (V volts) is given by,

$$V = \frac{Ee\ G}{32\ C}$$

where e = electronic charge (volts), G = gas gain, and C = integrating capacitance (farads), the maximum pulse amplitude for ^{14}C beta particles (E max. 158 KeV) is/

is $\leqslant$ 350 mV. To allow optimum ^{14}C detection the discriminator gates were set to cover the ranges, 2 to 20 mV, 20 to 400 mV, and greater than 400 mV. Thus channels 1 and 2 were used to record ^{14}C beta events while channel 3 monitored the high energy pulses associated with alpha particle emission. A threshold of 2 mV (approximately 1.6 KeV) was necessary to avoid the measurement of spurious noise pulses, which arose both from the counter electronics and as 'pick up' from other electrical equipment in the immediate vicinity.

(b) Operating voltage and gas characteristics: The voltage required to produce a predetermined gas gain is a function of both filling pressure and gas purity. The measured variation of working voltage with filling pressure is shown in Fig. 15 for pure CO_2.

Slight variations in CO_2 purity were unavoidable. Trace quantities of electronegative impurities in the counting gas decrease the electron multiplication and hence the distribution and amplitude of pulses in adjacent energy channels. A constant gas gain for all samples was achieved by adjusting the operating voltage to give a fixed pulse amplitude distribution between adjacent energy channels. For routine filling pressure (760 mm Hg at 15^{o}C) the operating voltage was in the range 3.48 $\pm$ 0.05 KV. The determination of operating conditions

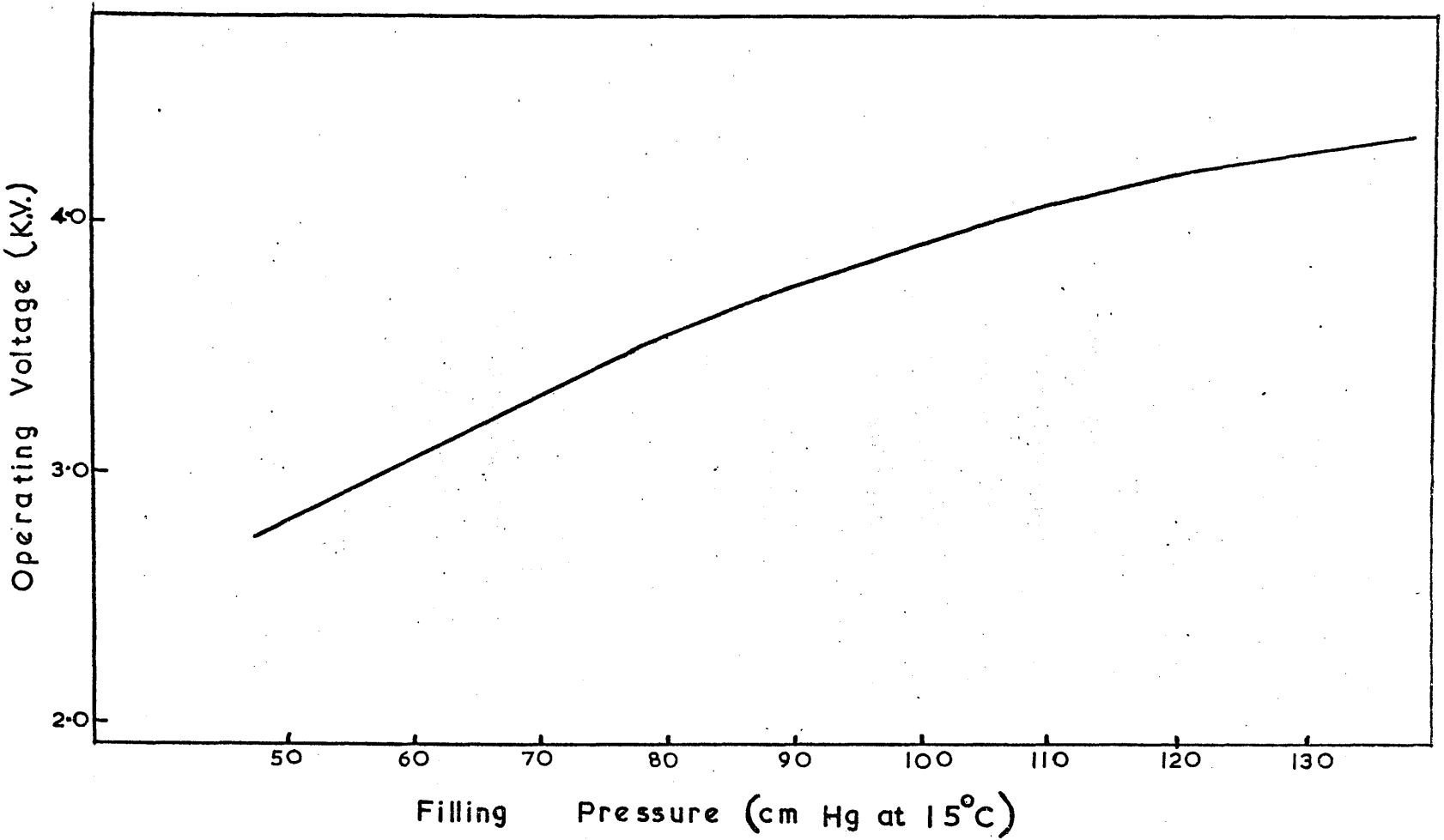
by/

Figure 15. Variation of Operating Voltage with Filling Pressure

GAS CO_2

ANODE DIAMETER 1 ml.

GAS GAIN 5×10^3



by pulse energy analysis required a source of constant energy which had a uniform flux through the detectors. The 'hard component' of cosmic radiation which penetrated the Pb shield exhibited these properties. The meson coincidence spectrum (Fig. 16) was, therefore, used to establish the operating conditions for each gas fill. A pulse distribution of 2:3 between energy channels 1 and 2 defined the necessary operating voltage. This pulse ratio was very sensitive to voltage adjustment since it corresponded to steep gradients in both differential energy curves.

The anticoincidence pulse distribution (Table 8) was not suitable for determination of the operating conditions due to both the low counting rate, and the varying proportion of the background spectrum in different sample count rates.

Outgassing of impurities from the counter walls and teflon insulators occurred during each counting sequence. This effect was evident from a gradual increase in the meson coincidence ratio with counting time. However, for counting periods less than 4000 minutes the effect on the overall counting efficiency was negligible. The original gas purity was regained after distillation of the CO_2.

Figure 16. Coincidence Meson Spectrum.

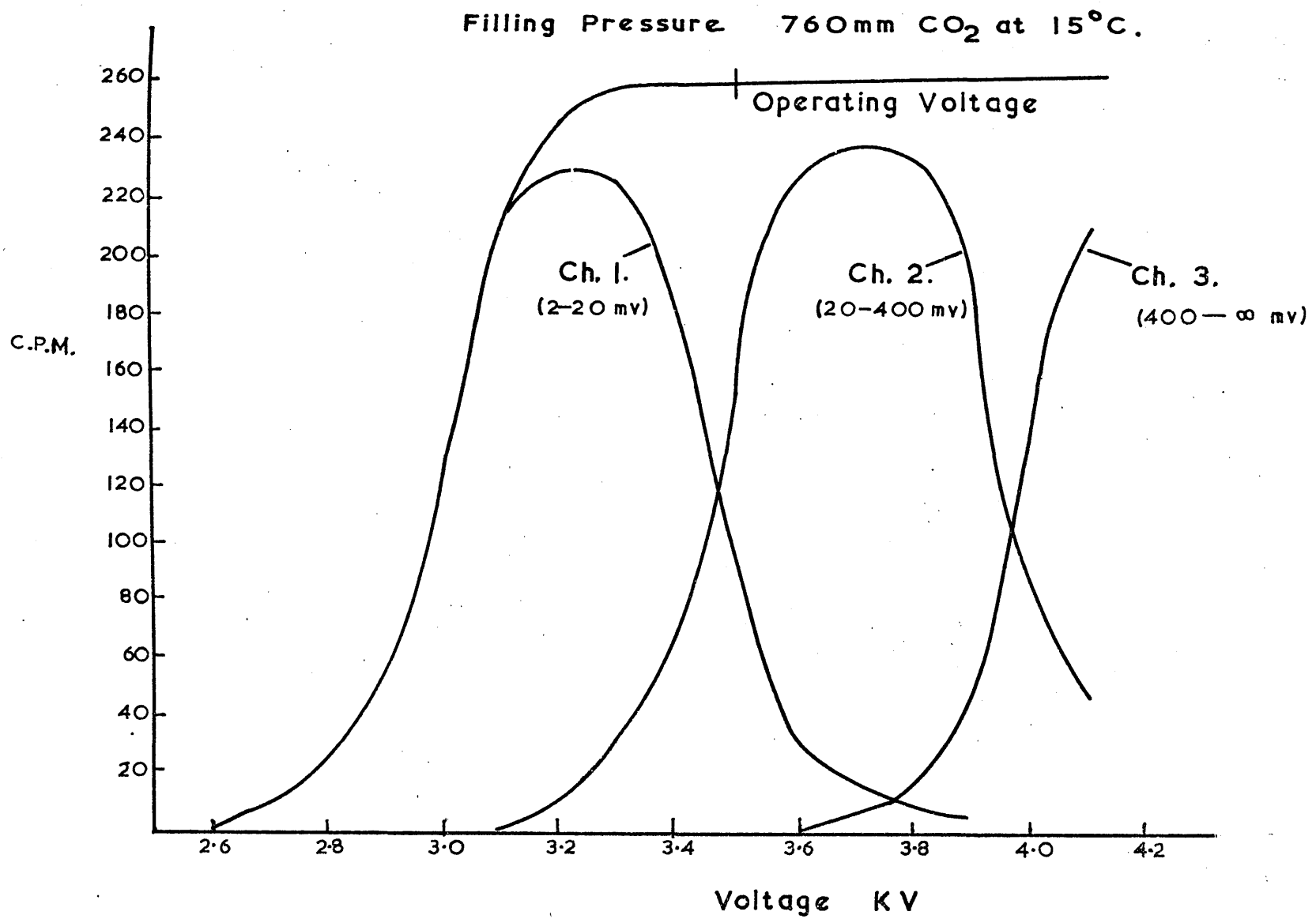


TABLE 8. Distribution of Anticoincidence Events.

ENERGY CHANNEL	1 (2 - 20mV)	2 (20 - 400mV)	3 (400 - mV)
SOURCE	% OF TOTAL COUNTS PER CHANNEL		
^{14}C as CO_2 in detector	27	73	0
Background, non active CO_2	29	70	1
^{222}Rn in equilibrium with its daughter products	23	38	39

(c) Counter stability: Counter stability was monitored through the measurement of either a background or a modern standard gas each week.

In some cases small, but statistically significant, changes in the ^{14}C detection efficiency occurred after maintenance operations on the equipment. Therefore, the gas counting programme was divided into periods which were determined by the statistical (2σ) agreement between consecutive measurements of the background and/or standard gases (Fig. 17).

2.7. ^{14}C Data Processing

As described previously all gases were counted under constant filling pressure and gas gain conditions. A typical log entry shown in Fig. 18 describes the operational procedures involved for each counting sequence.

(a) Background count rate: Measurements were made fortnightly with a minimum of 6000 counts recorded per run. A linear relationship was evident between the background count rate and barometric pressure. The linear regression for any series of data was calculated by computer analysis using the method of least squares fit. Such an analysis is shown graphically in Fig. 19, and the corresponding calculations are detailed in Appendix I.

Three regression analyses, each applicable to a particular/

Figure 17. Counter Stability Control Chart.

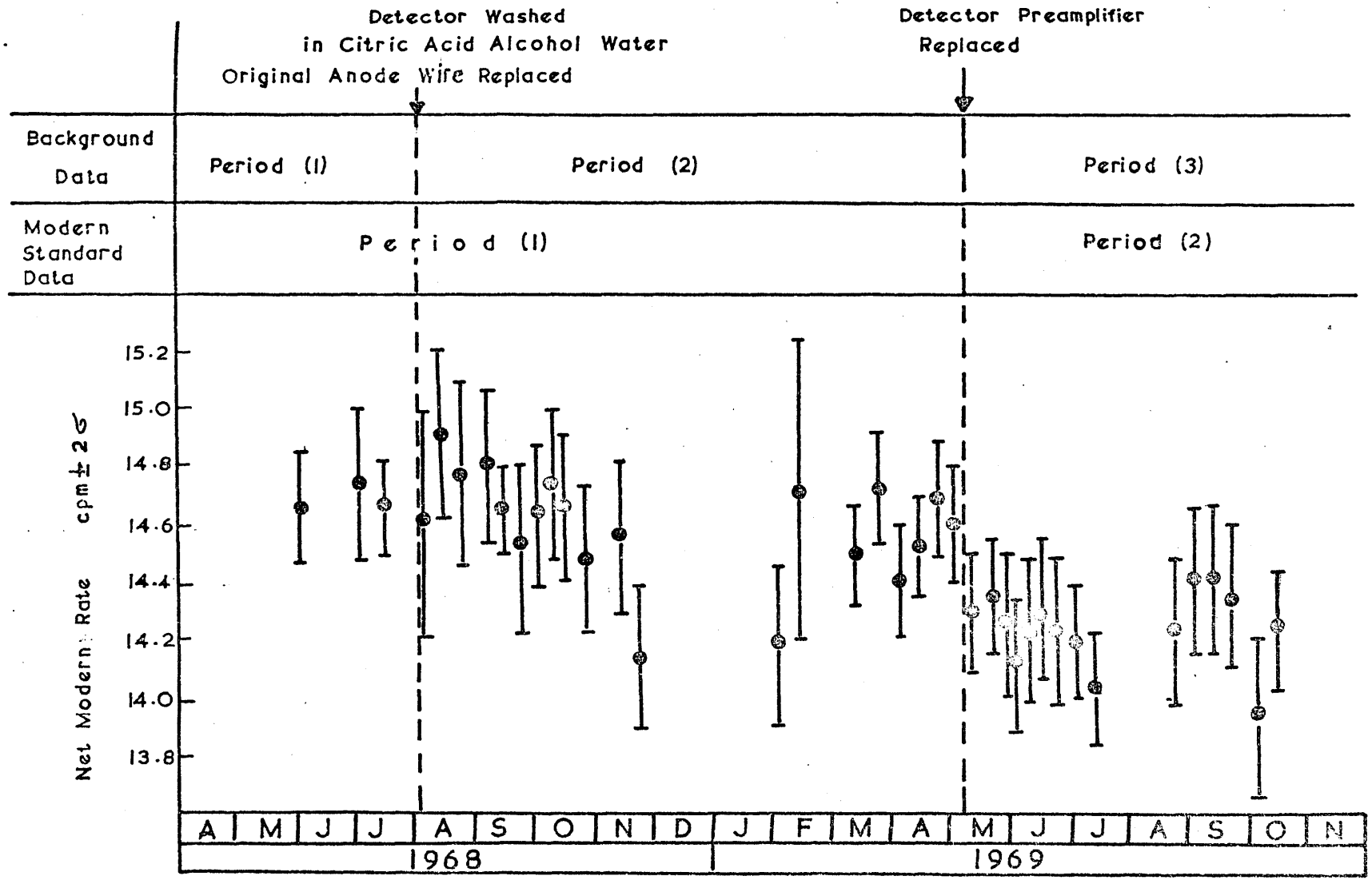


FIGURE 18. COUNTER LOG FORMAT.

SAMPLE Oxalic Acid Standard

DATE 13.10.69

GAS NO. 86/M

FILLING PRESSURE 77.6cm at 21°C

COINCIDENCE MESON SPECTRUM (cp2m)

EHT(KV)	C_1	C_2	C_3	C_T
2.6	6	-	-	6
2.8	43	-	-	43
3.0	251	1	-	252
3.2	473	23	-	496
3.4	402	143	-	545
3.6	75	450	4	529
3.8	27	469	31	527

GUARD VOLTAGE 1.31 KV

GAS FLOW RATE 30ml/min.

INITIAL GUARD RATE 700 ± 17 cpm

FINAL GUARD RATE 727 ± 17 cpm

COINCIDENCE MESON SPECTRUM (cp10m)

	C_1	C_2	C_3	C_T	$C1/C_2$
INITIAL	996	1596	1	2592	0.624
FINAL	1066	1630	2	2698	0.654

DETECTOR OPERATING VOLTAGE 3.50 KV

TIME ON 15.00 hrs 13.10.69 TIME OFF 09.20 hrs 14.10.69

TOTAL COUNTING TIME 1100 minutes

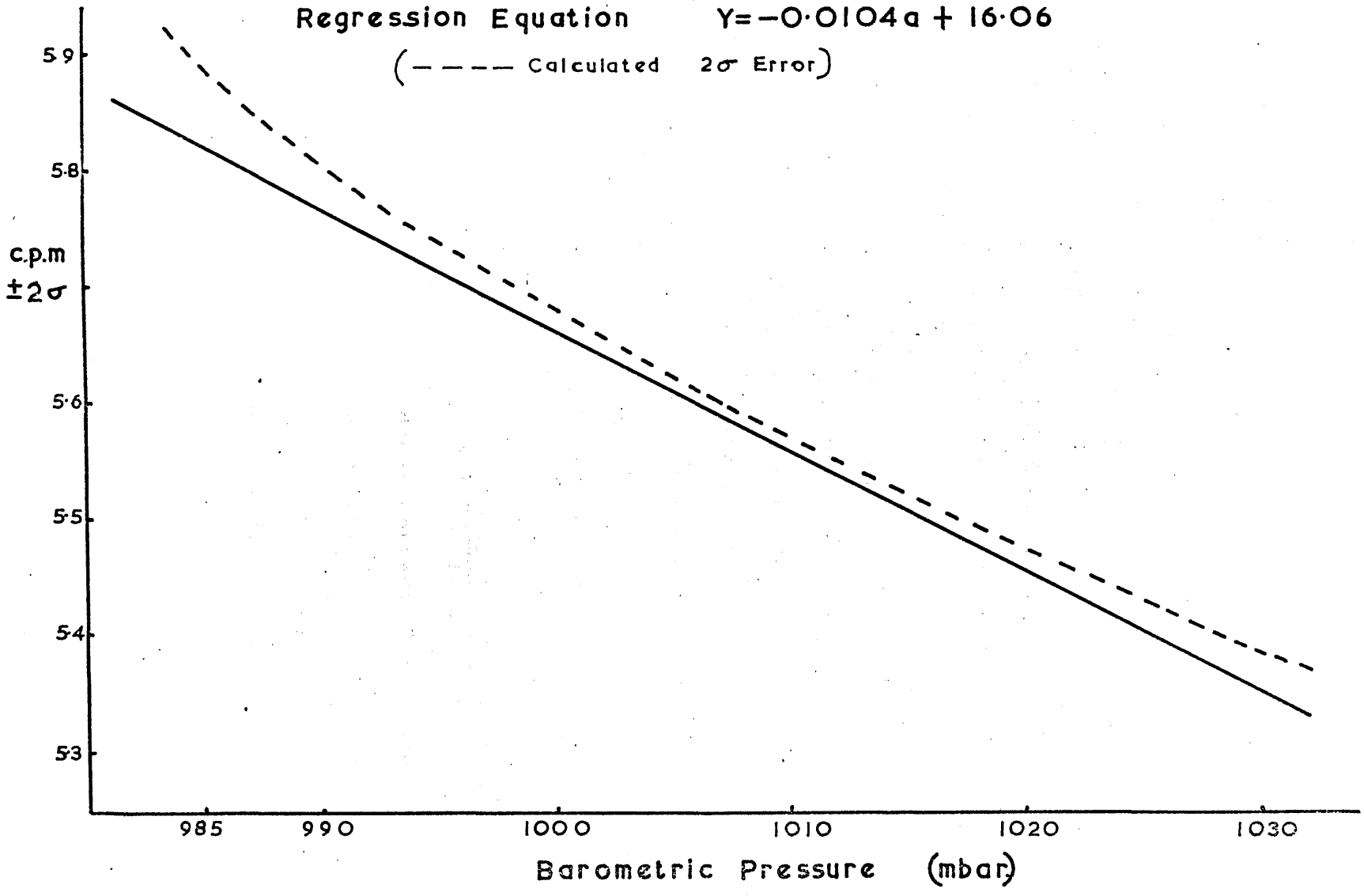
ANTICOINCIDENCE COUNT RATE

	A/C_1	A/C_2	A/C_3	A/C_T
TOTAL COUNT	6012	15811	40	21863
Cpm $\pm 2\sigma$	5.47 ± 0.14	14.37 ± 0.23	0.04 ± 0.01	19.88 ± 0.27

Rn CORRECTION - Nil.

^{14}C ACTIVITY (cpm $\pm 2\sigma$) 19.88 ± 0.27

Figure 19. Variation of Background Count Rate with Barometric Pressure.



particular counting period, have been used in calculation of the ^{14}C concentrations determined during this study (Fig. 17).

(b) Modern standard count rate: Where possible measurements were made weekly with a minimum of 20000 counts recorded per run. The net anticoincidence rate was calculated by subtraction of the appropriate background level.

For a given counting period a mean net anticoincidence rate was determined for all runs which agreed within $\pm 2\sigma$ counting error. The final modern standard count rate was derived from the mean value after corrections for radioactive decay and isotopic fractionation viz.,

(i) the decay correction was applied relative to 1.1.58 (t_o), with a decay rate of 0.12 °/oo per year. Thus,

$$A^1 = A \left[1 + \frac{0.12\ (t - t_o)}{1000} \right]$$

where A^1 is the decay corrected activity (cpm) and A is the mean measured activity (cpm) at time t years.

(ii) The isotopic fractionation correction was based on the mean value of - 19 °/oo for $\delta^{13}C$ according/

according to Craig [1961]. Thus,

$$A_o = A^1 \left[1 - \frac{2(\delta^{13}C + 19)}{1000}\right]$$

where A_o is the final corrected modern activity (cpm), and $\delta^{13}C$ is the $^{13}C/^{12}C$ ratio in the CO_2 relative to that of the P.D.B. Chicago Limestone Standard.

A slight but significant degree of fractionation occurred during the $CaO \rightleftharpoons CaCO_3$ purification reaction. Since the modern standard gas required repurification after about 12 consecutive activity measurements a sample was taken for mass spectrometric analysis after each purification cycle.

Two counting periods relative to modern activity have been used in the calculation of ^{14}C concentrations made during this study (Fig. 17).

(c) Sample gas count rates: Each gas was counted at least twice and several days apart to give a minimum cumulative total of 50000 counts. The beta and alpha count rates and the mean barometric pressure were noted for each counting sequence. If ^{222}Rn was detected in the sample CO_2 a suitable correction for the beta activity of its daughter products was applied to the total anticoincidence/

coincidence count rate (Appendix II). The net anti-coincidence count rate was determined for each sample run by subtraction of the appropriate background rate. A mean value was then calculated for net counting rates which agreed within $\pm 2\sigma$ counting error.

(d) Calculation of ^{14}C concentrations: ^{14}C concentrations were calculated relative to 0.95 times the activity of The National Bureau of Standards oxalic acid standard, which is regarded as equivalent to the activity of age corrected 19th century wood.

^{14}C data are expressed both in terms of $\delta^{14}C$ % and Δ %. The former term has limited significance and refers to the measured ^{14}C concentration prior to correction for isotopic fractionation which may have occurred in the sample. Calculations were performed using the method prescribed by Broecker et al. [1961] viz.,

$$\delta^{14}C = \left[\frac{As\ f}{0.95\ Am} - 1 \right] 1000\ ^{o}/_{oo}$$

$$\Delta = \delta^{14}C - (2\,\delta^{13}C + 50)\left(1 + \frac{\delta^{14}C}{1000}\right)\ ^{o}/_{oo}$$

where As is the sample mean net anticoincidence count rate, Am is the modern standard mean net anticoincidence count rate, and f is the dilution factor applied in cases where sample dilution with non active CO_2 had occurred.

The limits of error for data collection were defined by the statistical confidence between corresponding measurements, $\pm 2\sigma$. Final ^{14}C concentration values are quoted to $\pm 1\sigma$ error, and this relates solely to the random uncertainties associated with sample, modern, background, and mass spectrometric measurements.

The error on $\delta^{14}C$ was calculated from the relationship,

$$\pm 1\sigma = \pm 1000 \left[\frac{As.f}{Am} \sqrt{\left(\frac{\sigma As}{A_s}\right)^2 + \left(\frac{\sigma Am}{A_s}\right)^2 + \left(\frac{\sigma f}{f}\right)^2} \right]$$

The error on Δ was calculated using the formula reported by Callow et al. [1965] viz.,

$$\pm 1\sigma = \pm \sqrt{\left\{ \left[1 - \frac{(2\delta^{14}C+50)}{1000}\right]\sigma(\delta^{14}C)^+ 2\left[1 + \frac{\delta^{14}C}{1000}\right] (\sigma^{13}C)\right\}}$$

(e) Age determination: To avoid confusion with past radiocarbon dates it is current practice to calculate ^{14}C ages relative to the Libby half-life of 5,568 years. These values are converted to dates based on the 5,730 year half-life through multiplication by the factor 1.03.

A sample age, T years, is defined by

$$T = 8033 \log_e \frac{1}{(1 + \Delta 10^{-3})}$$

where $8033 = t_{\frac{1}{2}}/0.693$.

Limits/

$$\text{Limits of age } (T+t_1,\ T-t_2) = 8033 \log_e \frac{1}{1+[\Delta \pm \sigma_{(\Delta)} 10^{-3}]}$$

where radiocarbon ages are expressed in years B.P., this refers to years prior to 1950.

(f) Intercalibration of Counting Technique: Prior to the collection of ^{14}C data a series of interlaboratory calibration samples (Table 9) were measured to check the validity of the CO_2 preparation and counting technique.

The modern atmospheric intercalibration samples were counted first as CO_2 then converted to CH_4 for counting in the alternative systems [Baxter 1969, and Ergin 1969]. Charcoal age determinations were made using CO_2 or CH_4 prepared by the individual operators.

Good agreement was obtained within statistical error, with the previously established radiocarbon laboratories.

TABLE 9. Intercalibration Results.

SAMPLE DESCRIPTION	MEASURING LABORATORY	$\delta^{14}C$‰ ± 1σ	$\delta^{13}C$°/oo ± 1°/oo	Δ‰ ±1σ	Age Years
Charcoal from Kilphedir hut circles	Lamont	-	-	-	2100 ± 80
	Glasgow Univ.1	-	-	-	1908 ± 60
	" " 2	-	-	-	2064 ± 55
	This lab.	21.6±0.7	-26.8	-21.3	1922 ± 78
Snowdon Collection of April 1968	Glasgow Univ.1	59.8±0.7	-21.3	58.7±0.8	-
	" " 2	60.5±1.1	-21.3	59.4±1.2	-
	This lab.	60.0±0.9	-21.3	58.9±0.9	-
Snowdon Collection of June 1968	Glasgow Univ.1	60.0±0.7	-20.5	59.7±0.8	-
	" " 2	61.2±1.0	-20.5	59.9±1.1	-
	This lab.	61.6±0.9	-20.5	60.2±0.9	-

CHAPTER 3. THE DYNAMIC STRUCTURE OF THE ATMOSPHERE

3.1. Introduction

The bulk of artificial ^{14}C produced to date has been introduced into the northern and equatorial stratospheres. From these regions of the atmosphere the ^{14}C has become distributed throughout the atmospheric, biospheric, and oceanic reservoirs by various mechanisms. Up to the present the theories advanced to explain the transport of 'bomb' ^{14}C in the atmosphere have depended largely on our knowledge of particulate movement and are still subject to controversy. It is clear, however, that for our subsequent assessment of ^{14}C variations in the biosphere we must understand these atmospheric processes. In this chapter, therefore, the various theories advanced to explain atmospheric motion are outlined and the implications for the present study of ^{14}C are examined.

Early studies of particulate radioactive debris suggested that because of the small particle size distribution of stratospheric debris the behaviour of gaseous and particulate products of nuclear weapons' testing would be similar. Basic considerations, however, suggest that this concept must be erroneous. Varying degrees of gravitational settling must in fact be considered/

considered for particulate debris [Junge et al. 1961]. Further the effective life of this radioactivity in the troposphere is limited to approximately one month by rainout and it is thus prevented from re-entry into the stratosphere. Gaseous $^{14}CO_2$, on the other hand, is not subject to these removal mechanisms and, as will be shown later, has an effective life in the atmosphere much longer than for particulates and is on the order of several years.

The rate of exchange for radioactive species between the stratosphere and the troposphere also appears to be a function of the altitude and latitude of production [Telegadas et al. 1969]. Due to the higher energy yields of the thermonuclear devices which produced a large proportion of the artificial ^{14}C this isotope was generally injected at higher altitudes than the bulk of particulate fission products. The dispersion rates for ^{14}C throughout the atmosphere are, therefore, likely to be somewhat different from those established for particulate radioactivity. On the other hand, the mixing patterns exhibited by ^{14}C are, however, more likely to be representative of the air motions.

3.2. Sub-division of the Atmosphere.

The total mass of 5.27×10^{21} gm air surrounding the earth has a density of 1.225×10^{3} gm/m^3 at ground level decreasing to 3.49×10^{-1} gm/m^3 at 60 Km altitude. Thus/

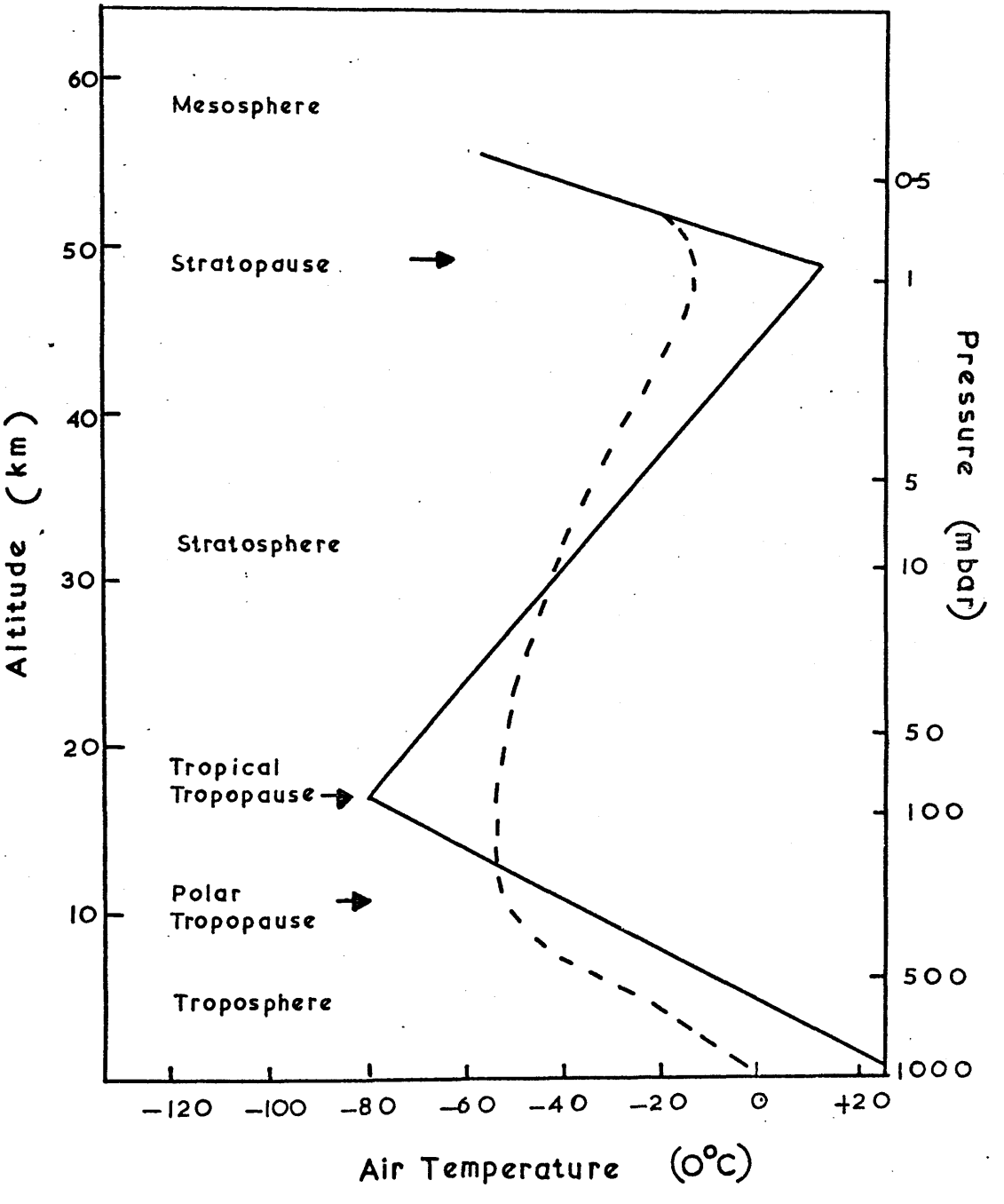
Thus 99.99% of the atmospheric mass of air lies below 60 Km. The chemical composition of dry air is 78.09% N_2, 20.95% O_2, 0.93% A, and 0.03% CO_2. Convection currents and diffusion processes maintain constancy of these molecular proportions at altitudes up to 60 Km. Additional components viz., water vapour, inert gases, and O_3 are present in variable trace quantities.

The movement of air within the atmosphere is controlled by the absorption and dissipation of solar energy. Consequently the atmosphere has a dynamic structure which is characterised by the temperature lapse rate i.e., the rate of change of temperature with altitude. The mean temperature structure as interpreted by Nicolet [1960] is shown in Fig. 20. A positive lapse rate denotes a decrease in temperature with increasing altitude, a negative lapse rate or 'inversion' describes the condition of increasing temperature with altitude.

(a) The troposphere: This lowest layer of the atmosphere contains approximately 82% of the atmospheric mass. It extends from ground level to altitudes of about 10 Km in the polar regions and about 17 Km in the tropics. It is deeper in summer than in winter, and, apart from these seasonal oscillations it is roughly symmetrical about the equator.

(b) The tropopause: This discontinuity marks the/

Figure 20. Vertical Temperature Structure of the Atmosphere.



the upper boundary of the troposphere. Often the transition from troposphere to stratosphere is abrupt and the tropopause can be identified as a surface. More commonly the transition is gradual so that the tropopause can only be defined as a layer several kilometers deep. The tropopause is not a continuous boundary but consists of several partially overlapping layers at altitudes which vary both with latitude and season. The tropical tropopause is virtually horizontal and relatively stable at about 17 Km. It extends from approximately 35^{o}N to 35^{o}S, being slightly higher and longer in the summer hemisphere. The polar tropopauses are more variable and exhibit large seasonal variations, high in summer and low in winter. Generally they slope upward from less than 9 Km in the polar regions to about 12 Km in the vicinity of 30^{o} latitude. The local altitude also varies with the constantly changing tropospheric weather systems. The polar tropopauses are low over cold air masses and cyclones, and high over warm air masses and anticyclones.

Gaps exist between the polar and tropical tropopauses and these constitute transition zones between tropospheric air on the equatorial side and stratospheric air on the poleward side. The latitude of the gap varies with season being closer to the pole in the summer hemisphere.

(c) The stratosphere: This region extends upwards from the tropopause to approximately 49 Km, where the temperature inversion reverts to a positive lapse rate at the stratopause. The temperature inversion is not uniform within this layer. Over the polar tropopause the stratosphere is nearly isothermal to about 23 Km whilst above this altitude the temperature increases to a maximum at the stratopause. Thus the stratosphere is often subdivided into upper and lower layers with the boundary at approximately 23 Km. Murgatroyd [1957] has shown that in winter the lower stratosphere poleward of 30^{o} is very probably a region of positive lapse rate, rather than an isothermal layer. Thus meridional subdivision of the lower stratosphere into polar and equatorial regions appears warranted.

3.3. Theories of atmospheric mixing.

Meteorological data show that the movement of air is predominantly zonal around the globe. The westerly circulation of the upper troposphere appears as a cyclonic vortex centered on the pole, with maximum wind velocities in the region of the lower tropopause gap. In summer this westerly component decreases rapidly above the tropopause, reverses, and becomes easterly throughout the stratosphere. In winter the pattern is similar for mid latitudes but in the polar region the westerlies increase with altitude to a maximum (the polar

stratospheric jet) in the upper stratosphere. The cyclonic pole-centered vortex of each hemisphere is not symmetrical but contains large waves which travel slowly eastward. The local wind direction is, therefore, constantly changing and significant meridional transport of air occurs.

The intensity of vertical mixing throughout the atmosphere is related to the temperature lapse rate. Thus in the troposphere where the decrease of temperature with altitude is large the atmosphere is unstable and turbulent vertical mixing is rapid. Meteorological studies have demonstrated the existence of a significant vertical/meridional circulation pattern in the equatorial troposphere viz., the Hadley cell. In this cell, air rises near the equator, moves polewards in the upper troposphere, descends in the regions 30^{o}N and 30^{o}S, and returns towards the equator in the friction layer near the earth's surface.

The non-uniformity of stratospheric inversion results in a corresponding variation in the resistance to vertical mixing. Throughout the year the tropical stratosphere has a stable inversion which strongly inhibits vertical transport. On the other hand the polar regions of the lower stratosphere tend to be almost isothermal and this corresponds to less stable stratification./

stratification. In winter the cooling effect and possible positive lapse rate of the lower polar stratosphere results in the most marked vertical stratospheric mixing. All regions of the stratosphere are, however, considerably more stable than the troposphere.

Throughout the atmosphere the longitudinal mixing rates are several orders of magnitude greater than meridional and vertical transport. Studies of the distribution of airborne radioactivity have shown that within a few weeks of input any longitudinal cross section of radioactivity is representative of the total atmosphere. The problem of artificial ^{14}C distribution, therefore, simplifies to an investigation of meridional and vertical mixing.

(a) Circulation models: The existence of an organised vertical/meridional circulation between the stratosphere and the troposphere was first postulated by Brewer [1949] in an attempt to explain low stratospheric humidities measured over the United Kingdom. A similar circulation was employed by Dobson [1956] to account for the distribution and seasonal variation of O_3 concentrations. This 'Brewer-Dobson' model proposes an ascent of air through the tropical tropopause, poleward transport within the stratosphere, and a descending motion towards the polar tropopause.

A theoretical calculation of a possible circulation

based on the conservation of atmospheric mass and energy has been reported by Murgatroyd et al. [1961]. This treatment is in close agreement with the 'Brewer-Dobson' model. Several variations of this general circulation pattern have also been proposed to explain the distribution and seasonal variations of particulate radioactivity concentrations, [Stewart et al. 1957, Libby et al. 1960 and Machta, 1965].

The basic objection to such organised circulation is the stability of the tropical tropopause. Murgatroyd et al. [1961] have computed an ascending air velocity of about 0.1 cm/sec through this region. These trajectory calculations imply that most of the air in the lower stratosphere cycles through the troposphere in one year. This does not seem to be the case since radioactive debris appears to be retained in the stratosphere for longer periods.

(b) Turbulent mixing theories: Turbulent or eddy diffusion is known to be associated with the global wind patterns. These processes must, therefore, be effective in the transfer of radioactivity from regions of high to regions of low concentration. The influence of these diffusion processes, often referred to as 'Austausch' can range over several kilometers.

The laws governing turbulent mixing are not well established/

established but nevertheless some attempts have been made to assess the mean vertical and horizontal diffusion coefficients in the atmosphere [Sutton 1953]. By analogy with the Fickian theory of molecular diffusion the concentration, Q, of an atmospheric tracer can be represented by a differential equation of the form,

$$dQ/dt = Ky \frac{d^2Q}{dy^2} + k_z \frac{d^2Q}{dz^2}$$

where y and z are the orthogonal coordinates in the meridional and vertical directions, Ky and Kz are the turbulent exchange coefficients in these directions, and t denotes time.

Probably the most successful application of this approach has been the analysis of the vertical profiles of stratospheric ^{185}W concentrations, [Feeley et al. 1960]. Values for the mean horizontal diffusion coefficient, Ky, were determined to be 5×10^8 to 5×10^9 cm^2/sec, and for the vertical diffusion coefficient, Kz, 10^3 cm^2/sec. These values are at best only a rough estimate of the mean diffusion rates. Since the rate of vertical mixing is related to the temperature lapse rate the values of Kz must show considerable variation with altitude, latitude, and season.

(c) Stratospheric/tropospheric exchange: Both circulation and diffusion theories can account for the transport/

transport of radioactivity across the tropopause. However, two additional mechanisms have been shown to be significant in the exchange of air across this boundary.

The tropopause is liable to disappear at one level and reform at a higher or lower altitude and hence when the tropopause rises by such a non-conservative process, stratospheric air is transferred to the troposphere without any vertical air motion having occurred. These vertical displacements of the tropopause result in a peeling away of radioactivity from the lower stratosphere. Staley [1960] has shown that this mechanism is particularly significant in the polar tropopause regions during spring.

Intrusions of stratospheric air into the troposphere by tropopause folding have been measured by Reed et al. [1959] and Danielsen [1965]. These injections of stratospheric air are associated with the regions of jet stream activity. It has been estimated by Reiter et al. [1965] that the annual exchange of air by this mechanism is equivalent to 30% of the total stratospheric mass.

Both these mechanisms can account for a large mass exchange between lower stratospheric and tropospheric air, especially at latitudes poleward of 40^{o}. The corresponding transfer of radioactivity must, however, be modified by the requirement for vertical transport within the stratosphere to convey the radioactive species to the vicinity of the tropopause.

3.4. Conclusions

The mixing of air among various regions of the atmosphere is clearly complex, and seasonal variations in these processes seem probable. The conflicting theories of atmospheric motion viz., large scale circulation or eddy diffusion, should, however, result in quite different dispersion patterns for ^{14}C injected into the stratosphere. If large scale circulation predominates excess $^{14}CO_2$ would be expected to exhibit the following trends.

(i) A general poleward movement throughout the stratosphere.

(ii) Confinement in the stratosphere to the hemisphere of production. (iii) Input to the troposphere throughout the year by transfer across the polar tropopause. If, on the other hand, eddy diffusion is a major mixing process the location, altitude, and season of ^{14}C production will have a significant effect. For ^{14}C introduced just above the tropopause or into the lower polar stratosphere during winter a relatively rapid and localised transfer to the troposphere might be expected. Production of ^{14}C at higher altitudes, however, should result in a more uniform and gradual tropospheric deposition since meridional dispersion would occur in the time required for the $^{14}CO_2$ to mix downwards to the vicinity of the tropopause.

CHAPTER 4. ^{14}C IN THE ATMOSPHERE OVER THE UNITED KINGDOM, 1967 - 69.

4.1. Introduction

To investigate the significance of atmospheric processes in the control of artificial ^{14}C levels over the United Kingdom the concentrations of this isotope in air from various altitudes were monitored during 1967 through 1969. CO_2 was collected from three regions; ground level, the upper troposphere, and the lower stratosphere. The sampling techniques employed have been discussed in Chapter 2.

4.2. ^{14}C in the Troposphere

(a) Collection programme: Three ground level stations were established viz., Chilton, Snowdon and Glasgow, and the results of concurrent ^{14}C concentrations at Lerwick (60° 08' N) were available from the work of Ergin [1969].

Chilton (51° 31' N. 1° 21' W) Collections were made in a rural area approximately 2 miles from A.E.R.E. Harwell. The wind direction at this site was variable but predominantly from the south east.

Snowdon (53° 03' N. 4° 0' W). The situation of this station, at 500 feet on the eastern slope of Mt. Snowdon, was ideal since it was remote from any local sources of CO_2 contamination. The prevailing wind direction was from the south west, therefore the air

over/

over this station was predominantly of oceanic origin.

Glasgow (55^{o} 58' N 5^{o} 0' W). Contamination by fossil fuel CO_2 from sources surrounding this site was soon evident in the measured data. Since the effect of localised ^{14}C dilution had no direct bearing on the present study measurement at this station was discontinued. It is interesting to note, however, that a subsequent investigation of this region performed by [Walker 1968] indicated that atmospheric contamination by 'dead' carbon could rise to 18%.

CO_2 from the upper troposphere was collected at altitudes within 2 Km of the tropopause. Whereas collections at ground level were on a cumulative monthly basis this CO_2 was collected during a 20 minute sampling period and could, therefore, be expected to indicate short term transfer of air across the tropopause.

(b) Results: The temporal variations measured in ground level air are presented in Figs. 21 and 22, and the (1σ) counting error associated with these data is $\pm$ 1%. Corresponding ^{14}C concentrations in the upper troposphere are given in Table 10.

(c) Implications of results: The data in Figs. 21 and 22 show marked seasonal oscillations in the mean ^{14}C concentrations of ground level air which are superimposed on a general decline of 3% to 4% per annum.

These/

Figure 21. Temporal Variations in ^{14}C Concentrations from Air Collected at Chilton (51°31'N 1°21'W).

(– – – – – Visual Aid Only)

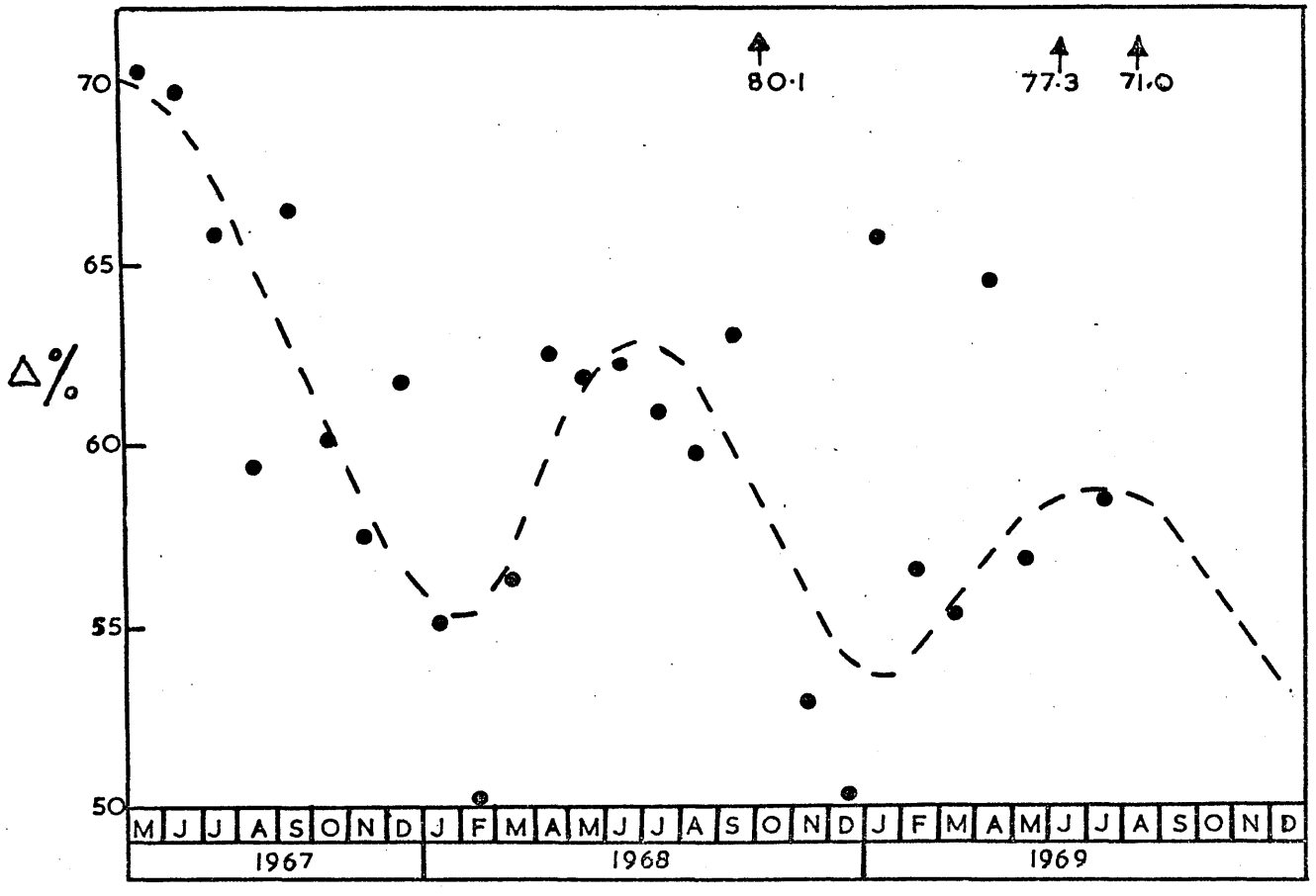


Figure 22. Temporal Variations in ^{14}C Concentrations from Air Collected at Snowdon (53° 03' N 4° 0'W)

(------ Visual Aid Only)

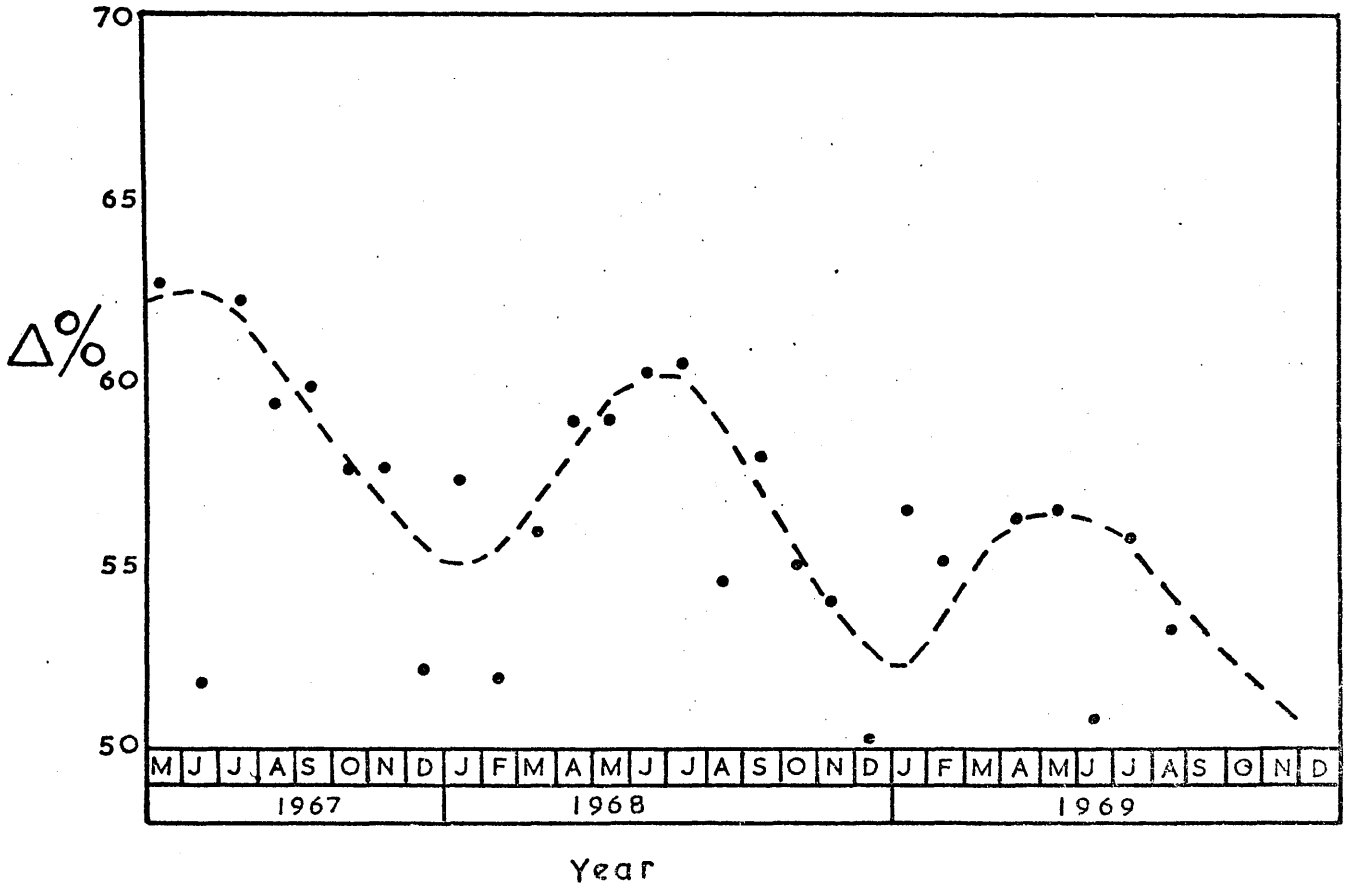


TABLE 10. ^{14}C Concentrations in the Upper Troposphere.

COLLECTION DATE	SAMPLING LOCATION	SAMPLING ALTITUDE Km	TROPOPAUSE ALTITUDE Km	^{14}C CONCENTRATION $\Delta\% \pm 1\sigma$	CORRESPONDING GROUND LEVEL CONCENTRATION $\Delta\% \pm 1\sigma$
15.1.68	52°N 01°W	8.9	12.8	54.6 ± 0.9	55.0 ± 1.0
15.2.68	53°N 01°E	9.5	10.7	55.8 ± 0.7	55.5 ± 1.0
5.3.68	54°N 01°W	11.6	12.8	56.2 ± 1.0	56.0 ± 1.0
19.3.68	54°N 02°W	7.6	8.5	63.0 ± 1.0	57.0 ± 1.0
26.3.68	52°N 0°W	10.7	11.6	60.8 ± 1.0	57.5 ± 1.0
26.4.68	53°N 01°W	8.9	11.9	61.6 ± 1.8	58.5 ± 1.0
30.4.68	53°N 01°W	8.2	8.9	60.4 ± 0.9	59.0 ± 1.0
4.10.68	51°N 06°W	11.9	12.8	56.1 ± 1.0	56.0 ± 1.0

these variations are in good agreement with the results of concurrent $^{14}CO_2$ concentrations monitored at Lerwick.

The variations in ^{14}C concentrations may result from a seasonal input of CO_2 from two sources namely, (i) a region of higher $^{14}CO_2$ specific activity viz., the lower stratosphere, during spring, or (ii) an increase in the rate of fossil fuel combustion viz., domestic consumption, during autumn and winter. It is unlikely that the latter source was the major contributor since the maximum turning points in ^{14}C concentration occurred during mid to late summer. Further, the variations in ^{14}C concentrations reported at these latitudes for previous years [Nydal 1965, 1967 and Münnich et al. 1967] show similar but more marked seasonal oscillations which were undoubtedly caused by the injection of high specific activity $^{14}CO_2$ from the stratosphere. That the lower stratosphere was still active in this respect during the period of this investigation will be shown later in this chapter. The effect of increased fuel combustion in adjacent urban regions allied with prevailing wind direction may, however, be reflected in the low ^{14}C concentrations measured in isolated winter collections at both Chilton and Snowdon.

The random occurrence of high ^{14}C concentrations at Chilton must be interpreted as localised contamination from/

from adjacent A.E.R.E. Harwell. Ergin [1969] has reported similar, but less frequent, high ^{14}C concentrations (approximately 70‰ Δ) at both Lerwick and Gibraltar. These anomolous values tended to occur during autumn and could possibly result from the localised transfer of stratospheric air to ground level via tropopause folding. It is significant, however, that no such high ^{14}C concentrations were detected at Snowdon.

^{14}C concentrations in the upper troposphere during 1968 (Table 10) show measurable seasonal differences from the corresponding ground level values. From mid March through April ^{14}C concentrations just below the tropopause were approximately 3‰ higher than those at ground level. Throughout the remainder of the year, however, good agreement existed between upper and lower tropospheric ^{14}C concentrations. This pattern for ^{14}C distribution in the troposphere would indicate that significant exchange of CO_2 across the tropopause at U.K. latitudes is limited to the spring months, and that at other times vertical homogeneity of tropospheric ^{14}C concentrations prevails.

4.3. ^{14}C in the Stratosphere.

(a) Collection programme: Collection of CO_2 from the lower 2 Km of the stratosphere was performed in/

in conjunction with sampling from corresponding regions of the upper troposphere. Thus, in addition to the establishment of ^{14}C concentrations in the lower stratosphere the localised exchange of $^{14}CO_2$ across the tropopause could also be studied.

(b) Results: The ^{14}C concentrations measured in stratospheric air are presented in Table 11. Fig. 23 shows these values relative to the corresponding ^{14}C concentrations measured in the upper troposphere and at ground level.

(c) Implications of results: ^{14}C concentrations in the lower stratosphere show a general decline of approximately 10% per annum during 1967 through 1969. The mean ^{14}C concentrations in this region were, however, still 10% to 20% higher than the corresponding tropospheric levels at this time.

The sharp decrease in ^{14}C concentrations in the lower stratosphere during the spring of 1968 corresponds to the increase noted in upper tropospheric ^{14}C levels (Fig. 23). The subsequent rapid rise in lower stratospheric ^{14}C concentrations would suggest that even higher ^{14}C concentrations existed at greater altitudes.

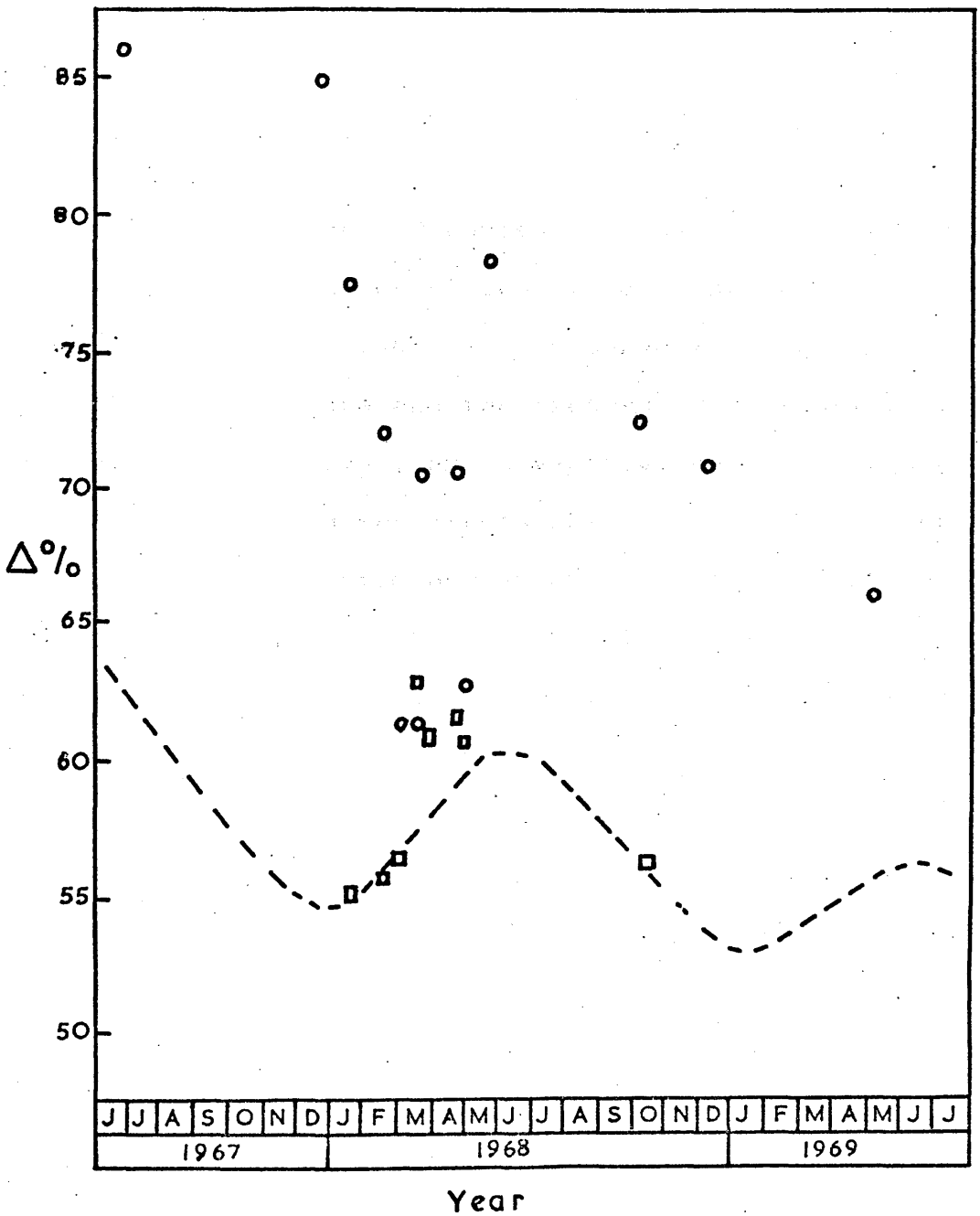
The retention of a marked concentration gradient for ^{14}C across the tropopause throughout most of the year would confirm that exchange of air between the stratosphere/

TABLE 11. ^{14}C Concentrations in the Lower Stratosphere.

COLLECTION DATE	SAMPLING LOCATION	SAMPLING ALTITUDE Km	TROPOPAUSE ALTITUDE Km	^{14}C CONCENTRATION $\Delta\% \pm 1\sigma$
30.6.67	58°N 2°W	12.8	11.9	85.9 ± 1.6
20.12.67	55°N 1°E	12.8	11.9	85.0 ± 2.1
15.1.68	49°N 2°E	13.1	12.8	77.5 ± 0.9
15.2.68	51°N 1°E	11.9	10.7	72.0 ± 0.8
5.3.68	53°N 2°W	13.1	12.8	61.4 ± 2.1
19.3.68	55°N 2°W	9.5	8.6	61.1 ± 0.9
26.3.68	51°N 2°W	12.8	11.6	70.6 ± 0.8
26.4.68	56°N 8°W	12.8	11.9	70.7 ± 0.7
30.4.68	57°N 4°W	11.9	8.9	62.8 ± 2.2
21.5.68	54°N 1°E	11.9	10.4	78.3 ± 1.7
4.10.68	58°N 6°N	13.7	12.8	72.7 ± 0.9
6.12.68	54°N 1°E	12.8	11.9	70.8 ± 0.7
8.5.69	50°N 5°W	13.1	10.1	66.1 ± 2.5

Figure 23. Variations of ^{14}C Concentrations in Air over the United Kingdom 1967–69.

(o – lower stratosphere, □–upper troposphere, ----- mean lower troposphere)



stratosphere and the troposphere is largely confined to the spring months at these latitudes.

4.4. Conclusions

It is clear that the burden of 'bomb' ^{14}C in the air over the U.K. is decreasing with time. By late 1969 the concentration of $^{14}CO_2$ in tropospheric air had declined to almost half the maximum levels registered during 1963-64. A more rapid rate of decrease had occurred in the ^{14}C concentrations of the lower stratosphere. (Δ values of 600‰ were recorded during 1963 [Godwin et al. 1964]). Homogeneity for ^{14}C between the stratosphere and the troposphere has still to be attained, however, and a vertical concentration gradient for ^{14}C within the stratosphere seems likely even in 1969.

The limited period of $^{14}CO_2$ exchange across the tropopause is more readily explained in terms of variable diffusion processes than by large scale circulation theories.

The occurrence of isolated low ^{14}C concentrations in air near ground level would suggest that fossil fuel CO_2 levels can be significant even in rural regions of the U.K. The alternation of tropospheric air masses of continental or oceanic origin over the U.K. may cause measurable short term fluctuations in the ^{14}C concentration of air at ground level.

CHAPTER 5. TRANSPORT OF ^{14}C IN THE ATMOSPHERIC RESERVOIRS

5.1. Introduction

From previous discussions it is evident that several mechanisms must be considered in the transport of atmospheric ^{14}C. In this chapter an attempt is made to assess the relative importance of these various mechanisms from investigations of the temporal variations in atmospheric ^{14}C concentrations during the period 1963 through 1969.

5.2. Temporal Variations in ^{14}C Concentrations

(a) The troposphere: Global variations in the ^{14}C concentrations of ground level air during 1963 through 1966 have been reported by several workers, [Fergusson 1965, Olsson et al. 1965, Rafter 1965, Lal et al. 1966, Nydal 1966, and Young et al. 1968]. Data for 1967 through 1969 were available from a world-wide network of sampling stations established by Ergin [1969], and from U.K. latitudes as described in Chapter 4.

Consideration of the availability of ^{14}C measurements and the magnitude of the meridional variations suggests that the troposphere may be treated/

treated as consisting of 6 latitudinal cells viz., $60^{o}N$ to $90^{o}N$, $30^{o}N$ to $60^{o}N$, $10^{o}N$ to $30^{o}N$, 0^{o} to $10^{o}N$, 0^{o} to $30^{o}S$, and $30^{o}S$ to $90^{o}S$. Mean monthly ^{14}C concentrations in each cell were calculated for the period 1963 through 1969 from the available data and the results are presented in Figs. 24 and 25.

From these results two features are readily apparent; (i) ^{14}C concentrations decrease steadily from north to south, and (ii) ^{14}C concentrations exhibit seasonal oscillations reaching maximum values during mid to late summer.

The tendency for the tropospheric ^{14}C concentrations to approach meridional homogeneity with time suggests that mixing by eddy diffusion processes is an important mechanism which is capable of mixing the total troposphere in less than 5 years. (Uniform ^{14}C concentrations, to within $\pm$ 5%, were attained throughout the troposphere by 1968 despite the steadily decreasing input of ^{14}C from the northern stratosphere).

Superimposed on the steady decrease of ^{14}C concentrations are the seasonal oscillations which suggest that the input of this isotope from the lower stratosphere reaches its maximum during spring and early summer. The work of Crutcher [1961] on

wind/

Figure 24. ^{14}C Concentrations in the Northern Hemisphere Troposphere.

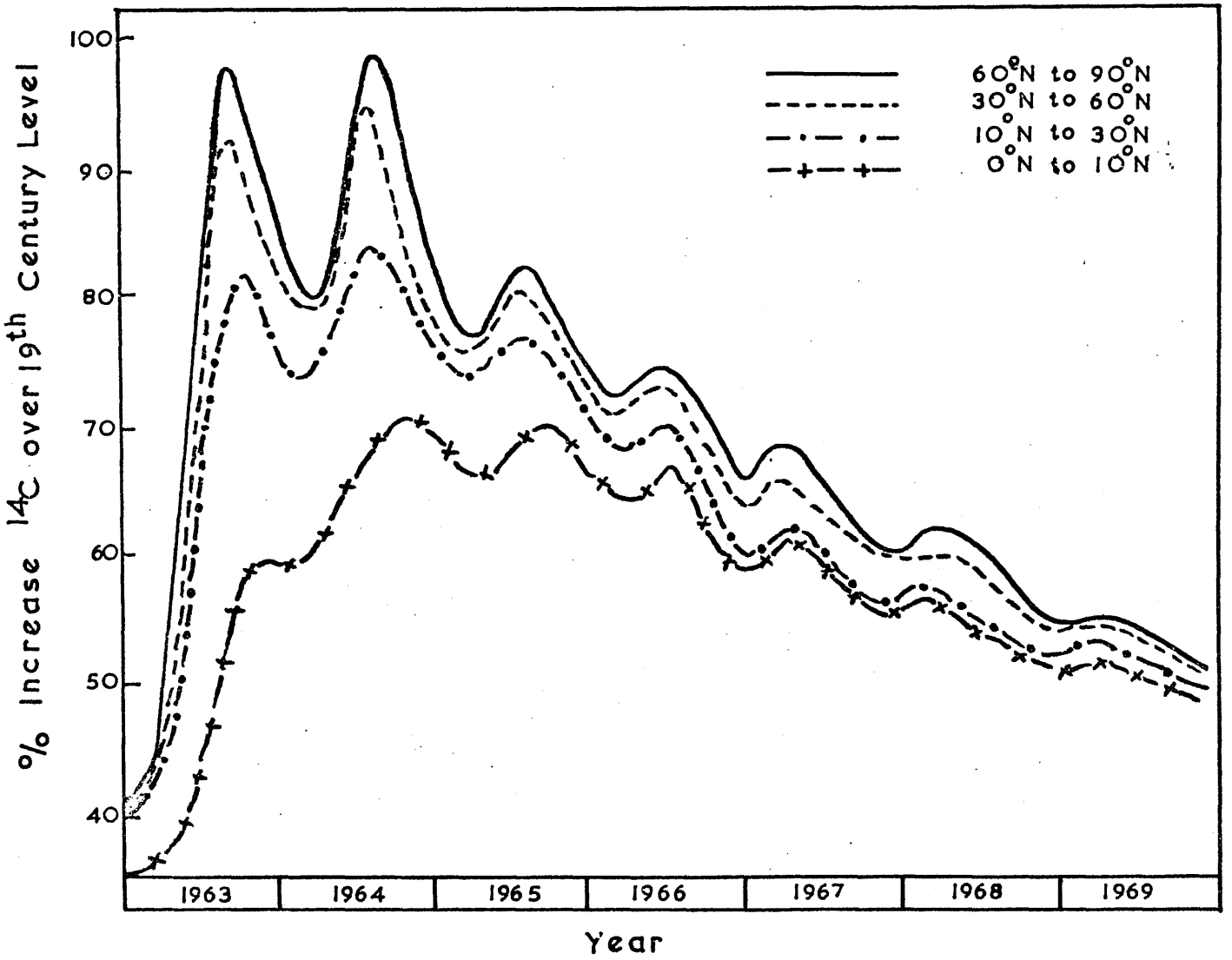
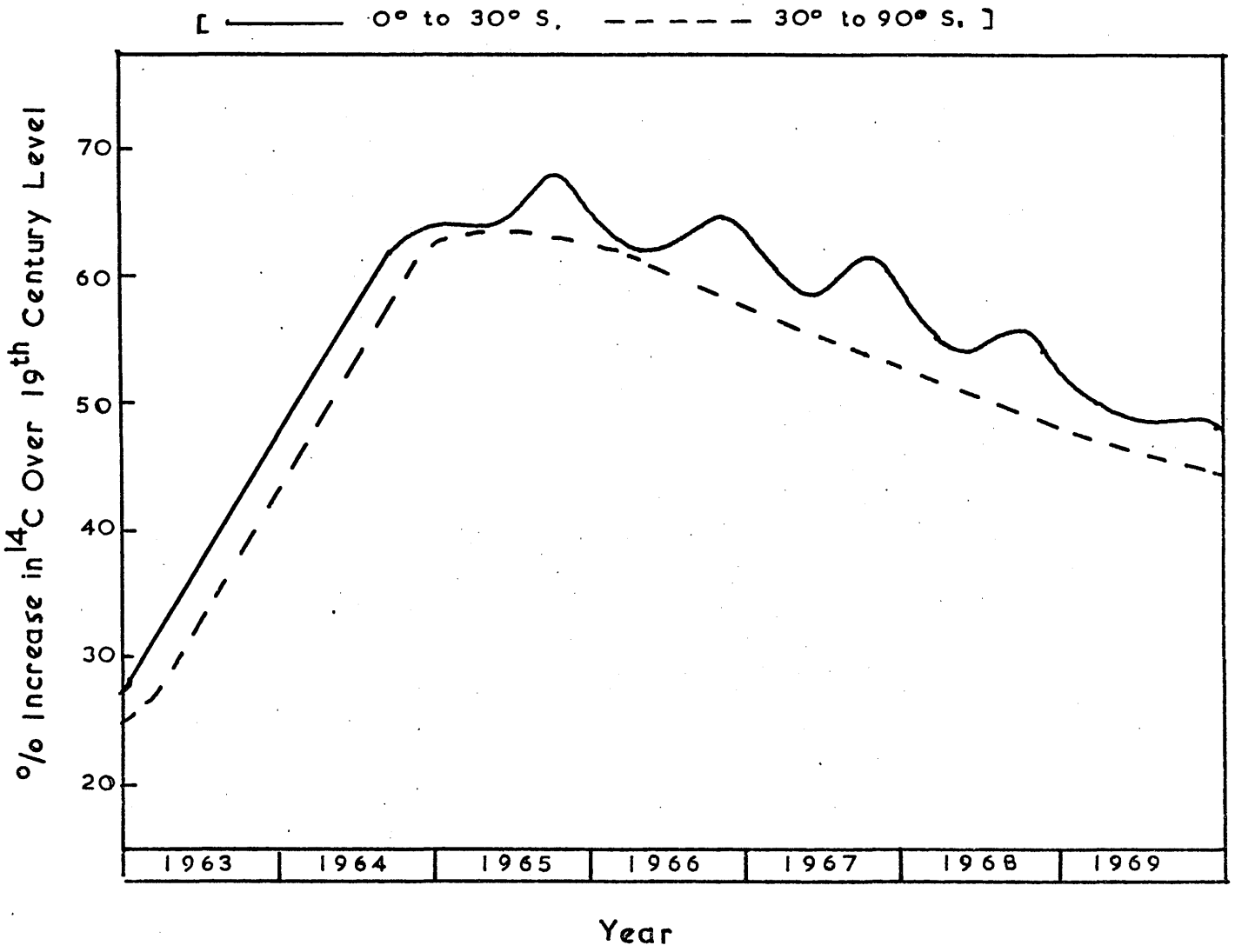


Figure 25. ^{14}C Concentrations in the Southern Hemisphere Troposphere.



wind velocities has shown that maximum meridional air motion occurs during autumn and winter. Thus the seasonal variations of the meridional eddy diffusion coefficients may well explain the observed ^{14}C variations. During the spring and summer the relatively low rates of meridional mixing coupled with the continuous input of ^{14}C from the lower stratosphere allows ^{14}C to accumulate at the latitudes of maximum stratospheric/tropospheric exchange. The marked decrease in this exchange and the increased meridional mixing during autumn and winter result in a net southward transport of ^{14}C.

(b) The lower stratosphere: Data reported by the U.S.A.E.C., Health and Safety Laboratory [1965, 1966, 1967, and 1969], have been used, together with measurements made during this study, to investigate the distribution of ^{14}C in this region. Preliminary examination of these data indicated that the stratosphere, in contrast to the troposphere, could not be considered well mixed even in 1968. This can be seen in the spatial distribution of ^{14}C in the northern hemisphere as a function of time as shown in Figs. 26 and 27. (These maps were produced from all ^{14}C values measured during the bimonthly periods January/February and July/August of each year. The ^{14}C concentrations/

Figure 26. Distribution of Excess ^{14}C in the Northern Hemisphere Lower Stratosphere (July / August 1966)

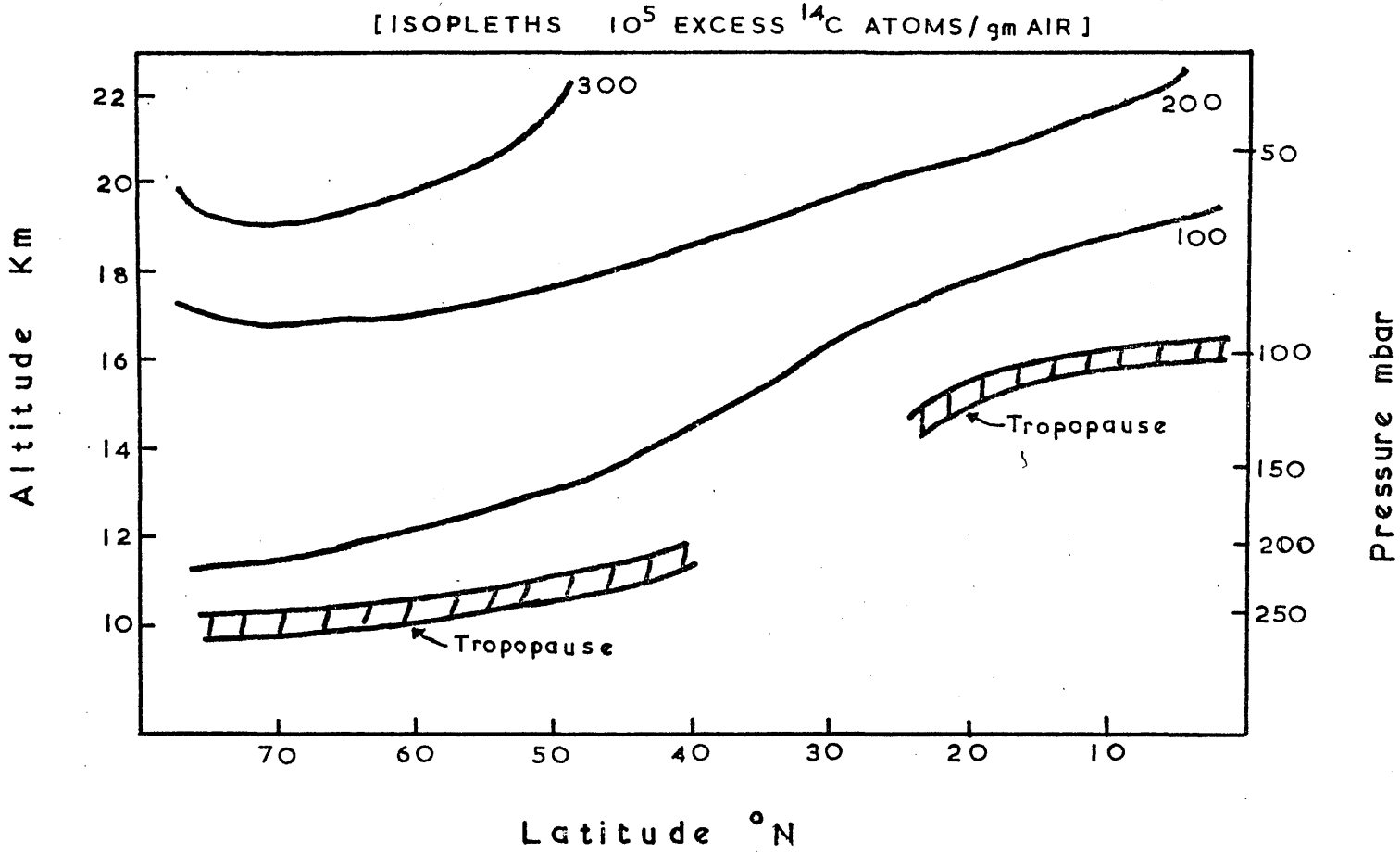
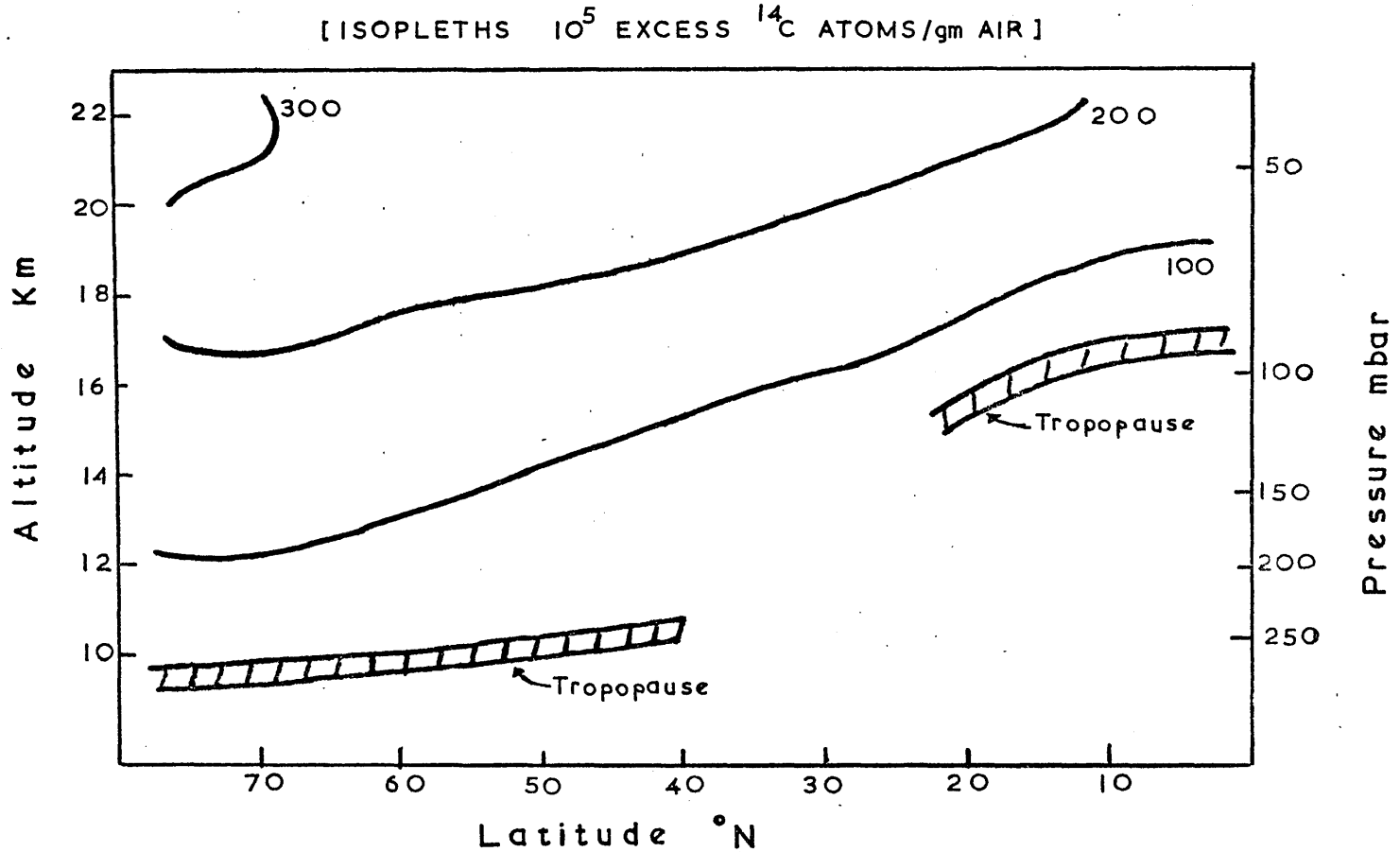


Figure 27. Distribution of Excess ^{14}C in the Northern Hemisphere Lower Stratosphere (January / February 1968)



concentrations have been arranged in a matrix (5^{o} latitude x 1.5 Km) and the array processed by computer [Batemann, 1969] to give isopleths at intervals of 10^{7} ^{14}C atoms excess/gm air.)

For the <u>southern hemisphere</u> ^{14}C concentration measurements reported by the U.S.A.E.C. were limited to the region $40^{o}S$ to $50^{o}S$. Profiles of the variation of excess ^{14}C with altitude were prepared, Figs. 28 and 29, and it was assumed that these were representative of the total region.

From the preceding figures the most significant features of the distribution of excess ^{14}C in the lower stratosphere are the constant altitude for maximum ^{14}C concentration and the tendency for the concentration gradients to run parallel to the mean tropopause height. This structure supports eddy diffusion rather than organised circulation as the primary mixing process. The behaviour of bomb ^{14}C is, therefore, best explained in terms of the Feely-Spar concept with horizontal diffusion several orders of magnitude greater than vertical diffusion.

An additional feature of the stratospheric data is that diffusion coefficients appear to vary with/

Figure 28. Profiles of Excess ^{14}C at 45°S. (1963 – 65).

(——— January / February. — — — July / August.)

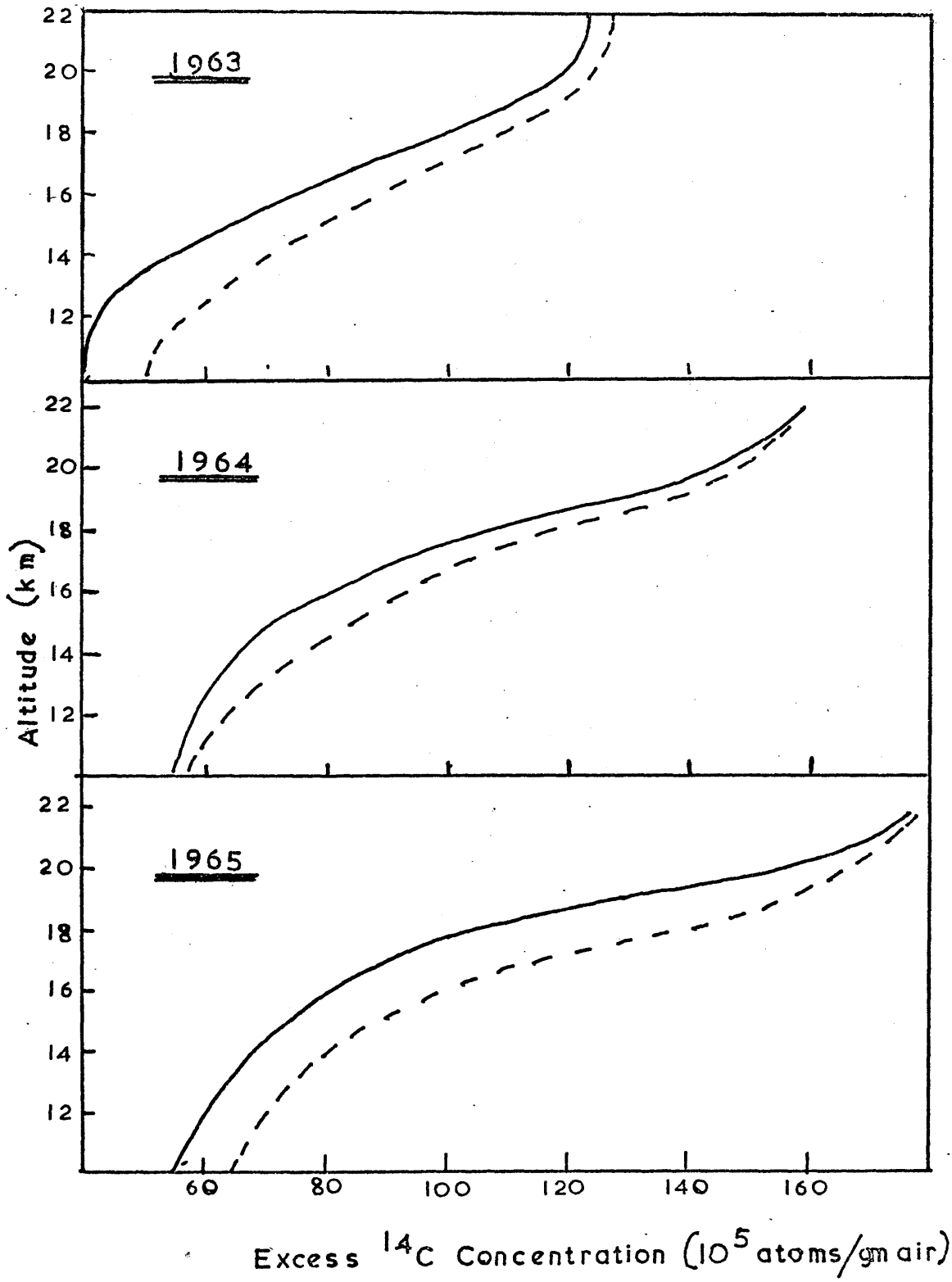
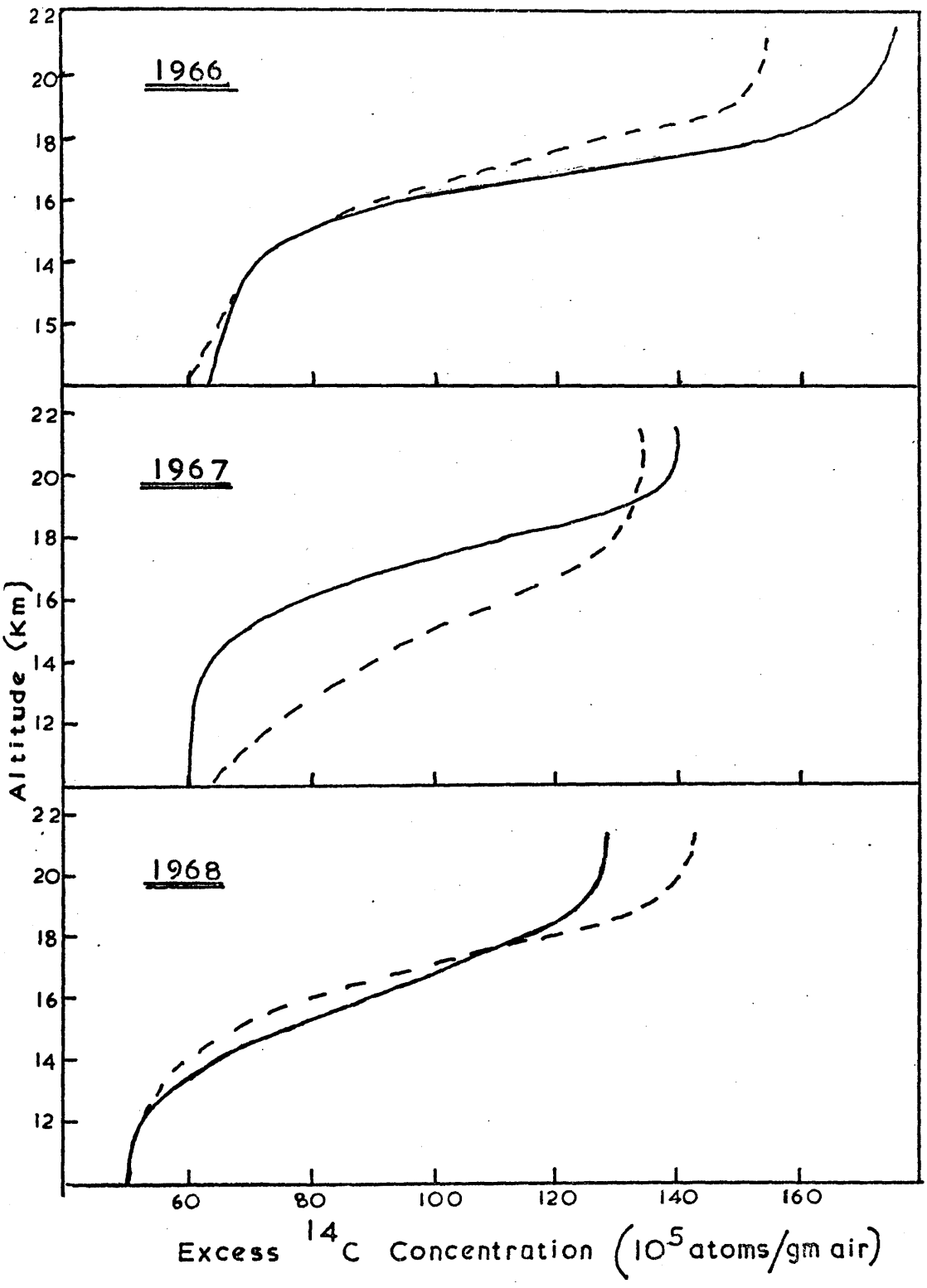


Figure 29. Profiles of Excess ^{14}C at 45°S. (1966-68).

(——— January/February. — — — — July/August.)



with both location and season. Contour plots, Figs. 30 and 31, indicate a downward transport of ^{14}C to the vicinity of the polar tropopause during the latter half of the year followed by a marked depletion of this region during the following spring. This behaviour is in general agreement with meteorological theories of increased vertical air motion during winter and early spring. A tendency for the isolines to bulge towards the tropopause gap is also evident. This would indicate increased horizontal diffusion in the region of the jet stream.

The southern hemisphere pattern shows a steady increase in ^{14}C concentration until 1965. Transport of ^{14}C from the northern hemisphere appears to be via horizontal diffusion at altitudes about 18 Km although the lack of data in this region naturally leads to this conclusion being rather speculative.

(c) The upper stratosphere: During the period 1963 through 1966 ^{14}C measurements for this region of the atmosphere were confined to random altitudes sampled in the vicinity of $30^{o}N$. Prior to, and during the 1959-60 test moratorium, however, a more extensive sampling programme was established for ^{14}C measurement at latitudes $70^{o}N$, $45^{o}N$, $32^{o}N$, $10^{o}N$, $32^{o}S$ and $45^{o}S$. The bulk of this ^{14}C had been introduced/

Figure 30. Distribution of Excess ^{14}C in the Northern Hemisphere Lower Stratosphere (January/February 1964)

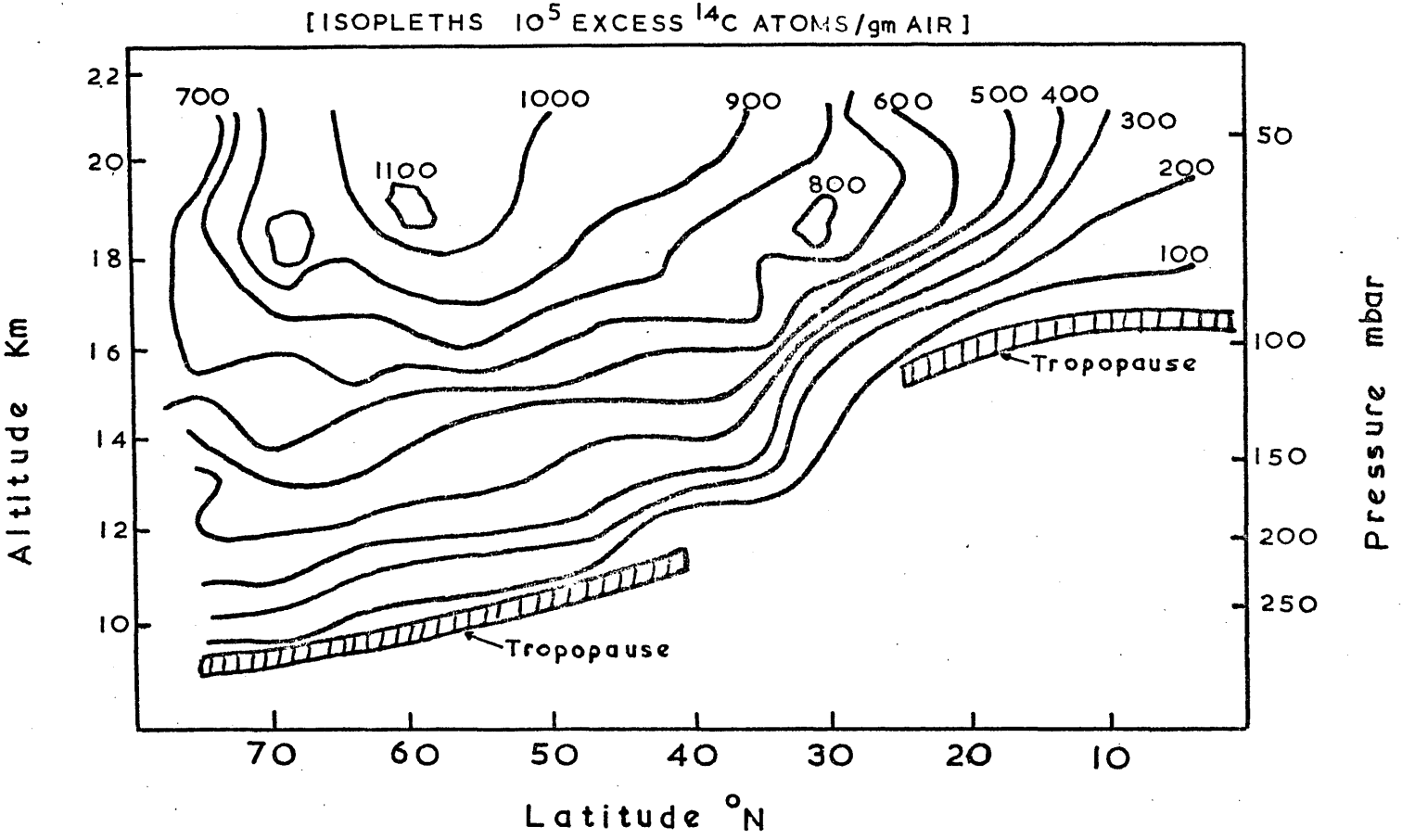
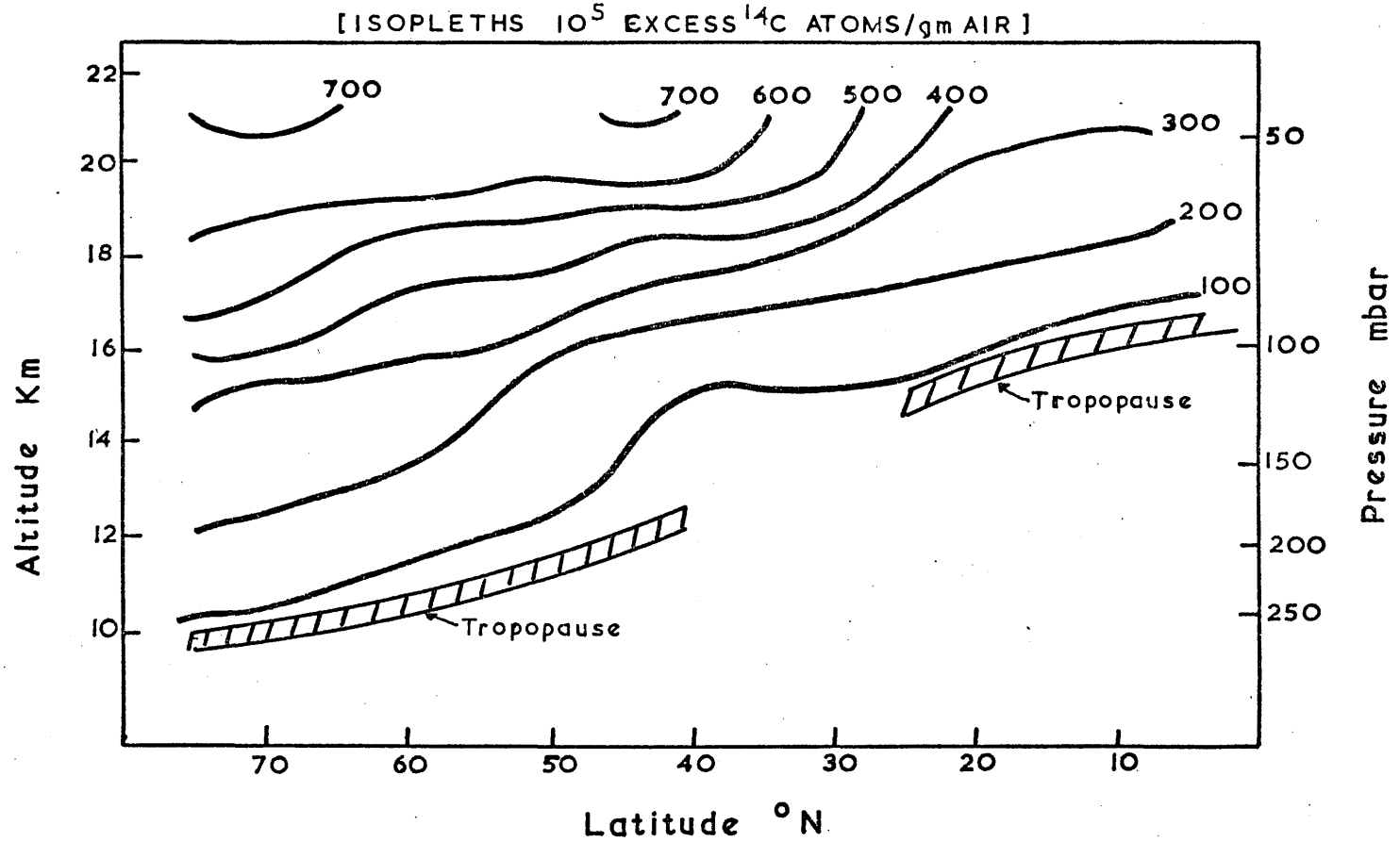


Figure 31. Distribution of Excess ^{14}C in the Northern Hemisphere Lower Stratosphere (July/August 1964)



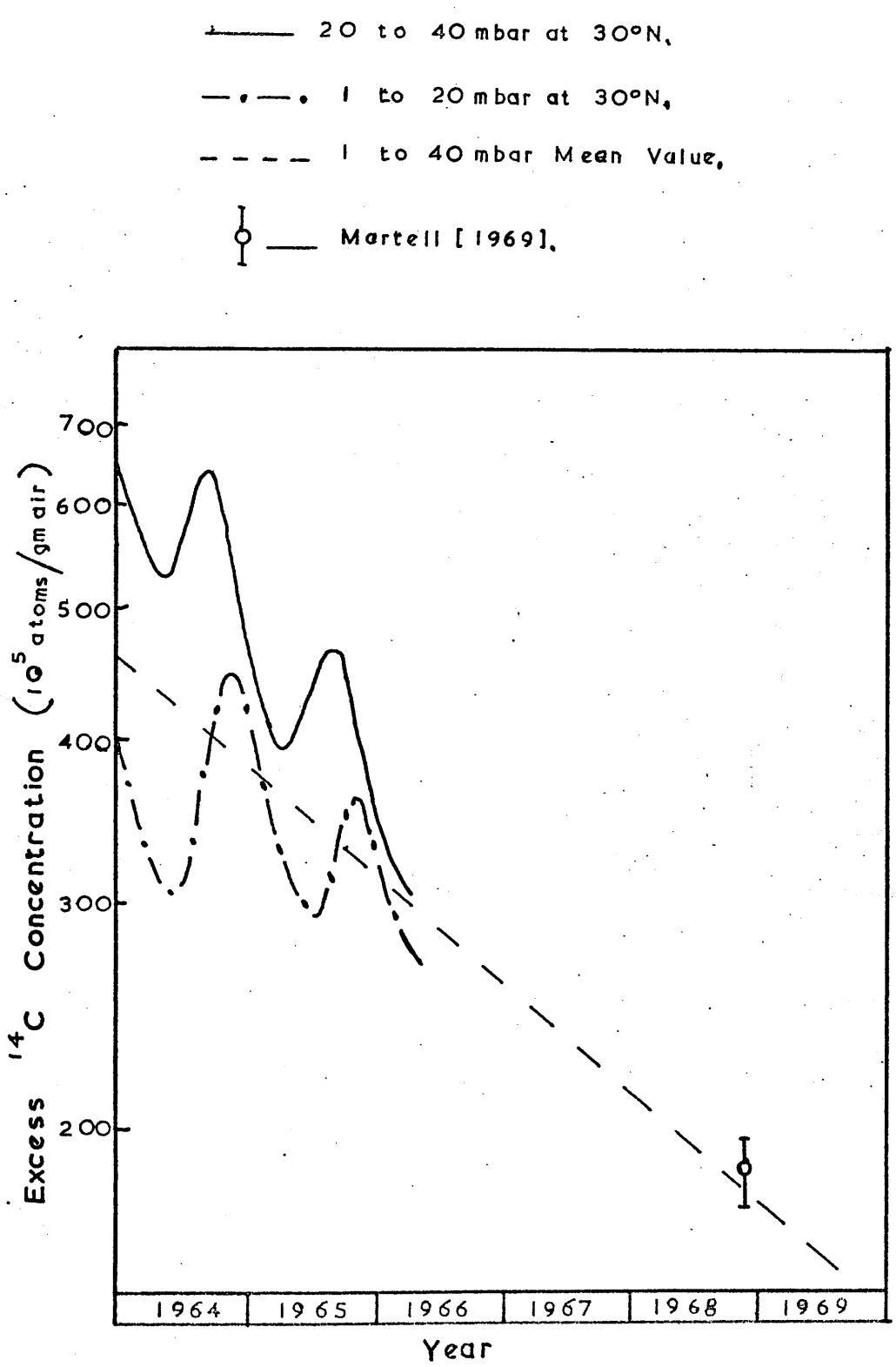
introduced into the equatorial stratosphere, and by late 1960 meridional homogeneity of ^{14}C concentrations was evident at all sampling latitudes. These earlier data indicate that meridional mixing is rapid in upper stratosphere and it was assumed, therefore, that from mid 1964 onwards the ^{14}C burden from the 1961-62 test series was also well mixed meridionally.

Extrapolation of the mean ^{14}C concentrations measured at 30°N during 1964 through 1966 (Fig. 32) shows good agreement with a recent measurement of excess ^{14}C in air sampled near the stratopause, [Martell, 1970]. The assumptions regarding meridional homogeneity in the upper stratosphere by mid 1964 would, therefore, appear valid.

^{14}C concentrations in the upper stratosphere for the period 1963 through 1966 retained a dynamic maximum at approximately 24 Km. The decrease in the mean ^{14}C concentration as a function of time was exponential with a half life of about 40 months and superimposed on this general decline was a seasonal fluctuation which appeared to vary with altitude. Above 24 Km the maximum ^{14}C concentrations occurred in the latter half of the year, while at lower altitudes the fluctuations were approximately 6 months out of phase. These seasonal oscillations

in/

Figure 32. ^{14}C Concentrations in the Upper Stratosphere.

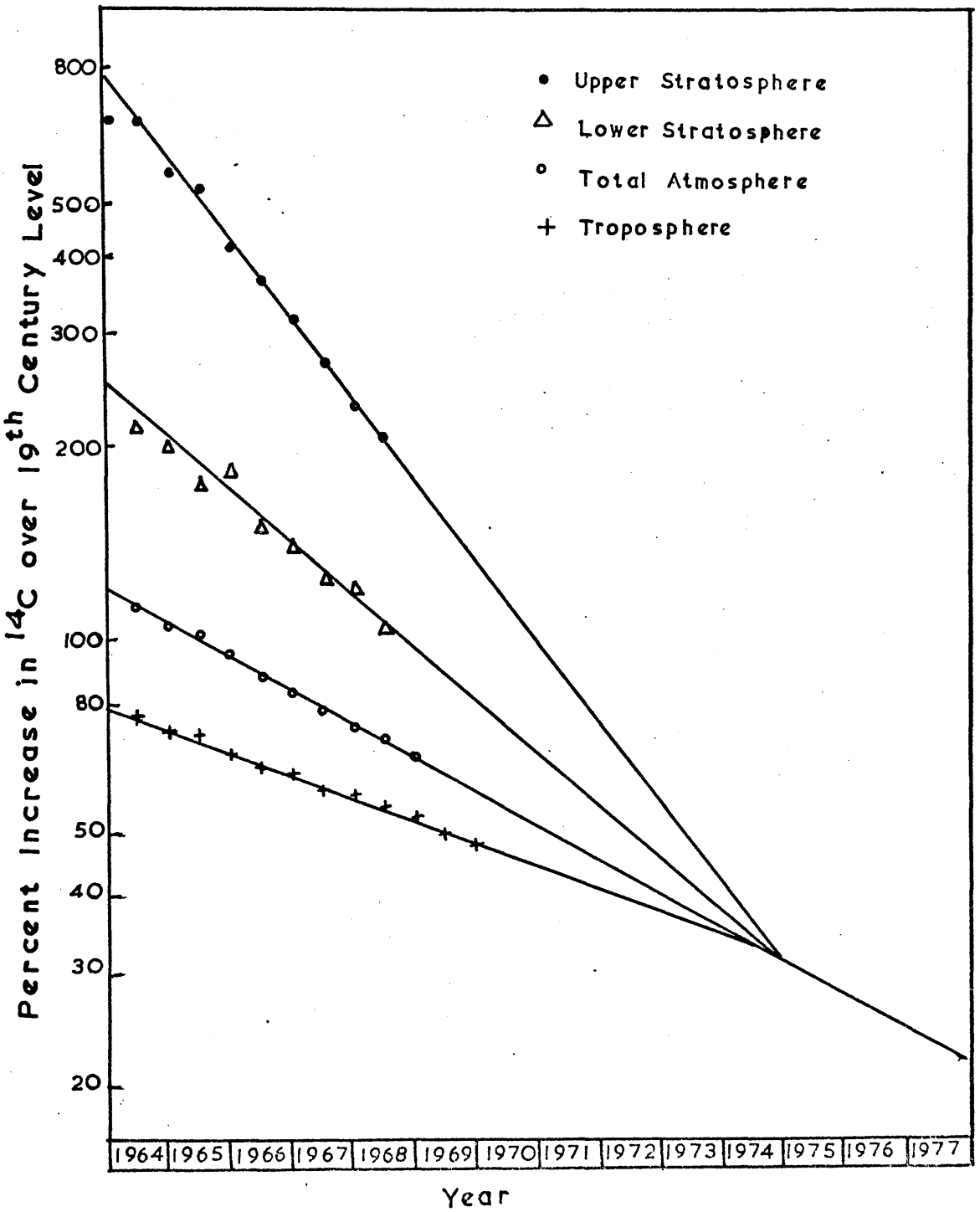


in ^{14}C concentrations indicate significant vertical air motion during spring which coincides with the period of maximum stratospheric/tropospheric exchange. It is interesting to note that a similar pattern for ^{90}Sr concentrations in this region of the atmosphere has been reported by Krey [1969].

(d) The total atmosphere: The temporal variations in atmospheric ^{14}C concentrations to date indicate that the atmosphere is tending towards uniform ^{14}C concentration. An overall decrease in the total ^{14}C burden in the atmosphere is also evident as CO_2 exchanges with the biosphere and oceans. The mean ^{14}C concentrations in the major regions of the atmosphere are presented in Fig. 33.

The ^{14}C concentrations in each region show an exponential decrease with time and extrapolation of the measured data for 1964 through 1969 suggests that in the absence of further artificial ^{14}C production uniform atmospheric concentrations will be attained within the next 5 years. A significant feature of Fig. 33 is the time required for complete atmospheric mixing of $^{14}CO_2$ viz., 12 years, relative to the apparent residence half time for a $^{14}CO_2$ molecule in the atmosphere viz., 5.5 years.

Figure 33. Temporal Variations in Atmospheric ^{14}C Concentrations.



5.3. Summary of Conclusions

The temporal and spatial variations in bomb ^{14}C distribution during 1963 through 1969 give strong support to the importance of the diffusion mechanism in atmospheric transport. Vertical and meridional diffusion rates are, however, extremely variable with both location and season. For limited tracer data these variations might well indicate a quasi-circulation pattern within the stratosphere and across the tropopause.

The transfer of ^{14}C between the stratosphere and the troposphere appears to result primarily from the displacement and distortion of the tropopause and from horizontal diffusion through the tropopause gap. The overall rate of transfer from the stratosphere to the troposphere is then dependent on the diffusion processes which transport $^{14}CO_2$ from higher levels in the stratosphere to the vicinity of the tropopause. Organised circulation across the polar tropopause is most unlikely in view of the ^{14}C concentration gradients which are maintained across this boundary during most of the year. (The fact that stratospheric/tropospheric exchange of $^{14}CO_2$ is largely confined to the period of maximum tropopause instability viz., February through April in the northern hemisphere, has been demonstrated in/

in Chapter 4.) Penetration of the tropical tropopause by the convective Hadley cell circulation cannot be disproved from the available ^{14}C data. If such transport exists, however, it is only effective in the lower 2 Km of the stratosphere.

CHAPTER 6. THE FUNCTION OF THE BIOMASS IN THE DYNAMIC CARBON CYCLE

6.1. Introduction

In this study the term 'biomass' is used to define the total quantity of biogenic material contained in the dynamic carbon cycle. Thus the biomass is distributed through both terrestrial and marine environments. An obvious division of this reservoir exists between the living matter (the biosphere) and the associated mass of decaying organic materials (humus).

Although the carbon content of the biomass is comparable with that of the atmosphere it has been disregarded or, at best, treated empirically in past studies of carbon transport. In many instances the biomass plus the ocean surface layer were considered as a single carbon reservoir. In studies which relate to fluctuations in the production rate of natural ^{14}C this approach seems justified since such changes were gradual. The biomass will, however, have a significant influence on the transient conditions arising from the rapid production of artificial ^{14}C in the atmosphere. Dyck [1965] has likened the biomass to a rapid circulating pump for atmospheric CO_2 with a cycling time/

time of approximately 20 years. The biomass appears to act therefore as a temporary sink for atmospheric CO_2 and as such will exhibit a damping effect on any rapid fluctuations in atmospheric ^{14}C concentrations.

Marked variations in the size of the biomass are known to have occurred during past geological time. Over the time interval of our present study, however, relatively little change will have occurred in the biogenic carbon in equilibrium with atmospheric CO_2.

Unfortunately, the data reported for the equilibrium masses of biogenic carbon (Table 12) and the rate at which this reservoir exchanges with the atmosphere (Table 13) are rather uncertain. The application of these data in model evaluations is further complicated by the diverse physical composition and the varied geographical distribution of this carbon reservoir. Seasonal and geographical variations in the rates of exchange of CO_2 with the atmosphere are also evident [Bolin et al. 1963, and Junge et al. 1968].

Despite these difficulties some approximate calculations can be made on the transport of 'bomb' ^{14}C through the biomass. In this chapter an attempt is made to establish an approach whereby the rate of this ^{14}C transport and its influence on both contemporary and future ^{14}C concentrations in the terrestrial/

TABLE 12. Estimated Inventories of Biogenic Carbon (10^{17} gmC)

TERRESTRIAL BIOSPHERE	TERRESTRIAL HUMUS	TERRESTRIAL BIOMASS	MARINE BIOSPHERE	AUTHOR
2.8	-	-	-	Borchert 1951
-	-	16.8	-	Libby 1955
2.5	10.2	12.7	-	Arnold et al. 1957
3.2	10.8	14.0	0.08	Craig 1957
1.2	7.1	8.3	0.1	Leith 1963
-	-	7.4 to 9.3	-	Leith 1969

TABLE 13. Estimated Annual Fixation of Atmospheric Carbon by the Terrestrial Biosphere (10^{16} gm C/year)

ESTIMATE (global)	AUTHOR	
2.0	Goldschmidt	1954
2.0 ± 0.5	Hutchinson	1954
1.5	Leith	1963
4.0	Junge et al.	1968
3.8 ± 0.6	Leith	1969
(poleward of 45° N)		
0.4	Bolin et al.	1963
0.5	Junge et al.	1968

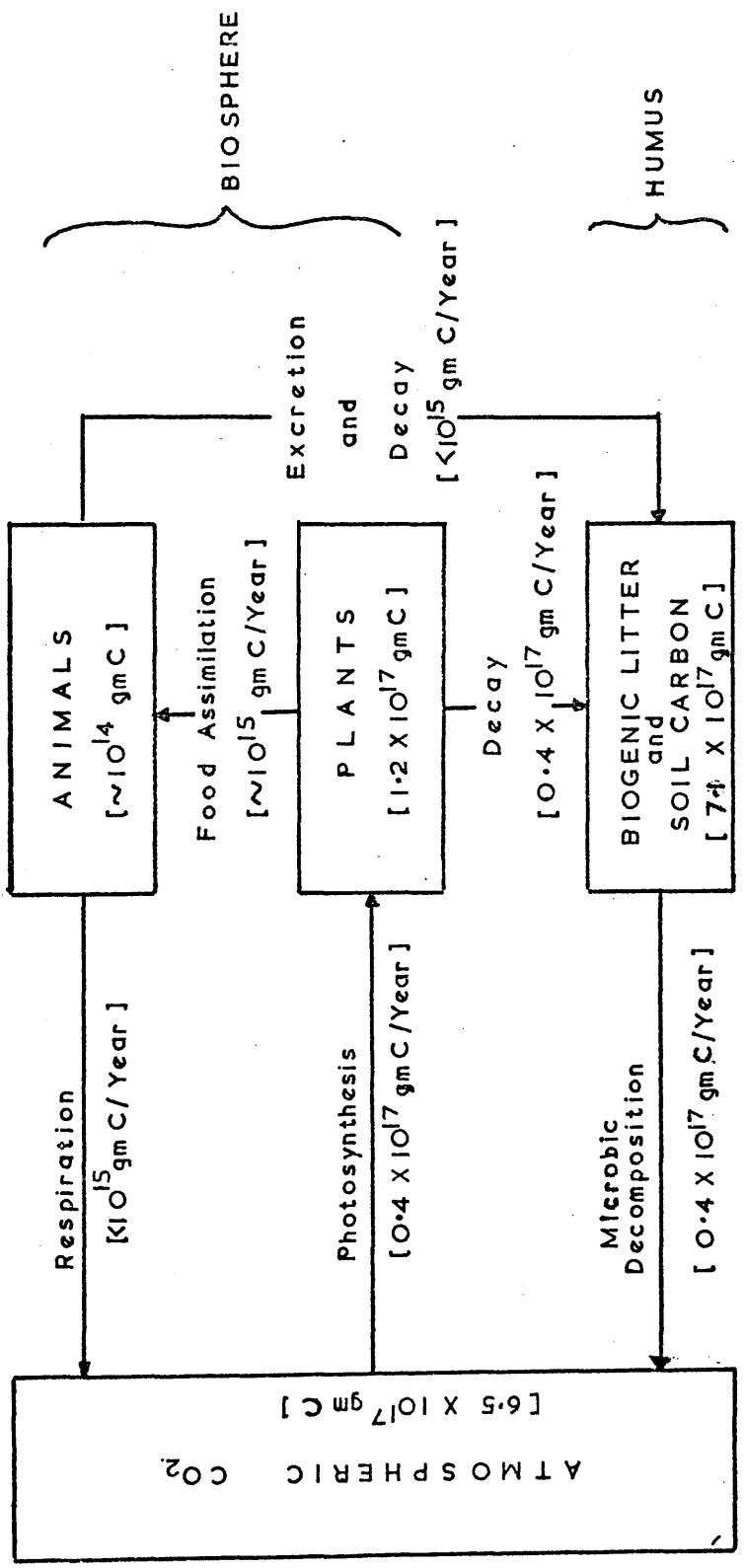
terrestrial carbon reservoirs may be assessed. (The role of the marine biomass is regarded as insignificant due to the 5000 % relative excess of inorganic carbon in the oceanic reservoir.)

6.2. The Transport of ^{14}C through the Biomass

(a) Model construction: The representation of the processes which occur in the exchange of CO_2, between the atmosphere and the biomass (Fig. 34) is based on the most recent data available [Lieth 1969]. From the relative masses of carbon involved only the metabolic action of plant materials viz., approximately 99% of the total exchange activity, need be considered in the present treatment.

The mean cycling time for a carbon atom through living structures can be estimated as 3 years from consideration of the mass of living carbon and the photosynthetic fixation rate for atmospheric CO_2. It should be realised, however, that wide divergence from this mean value occurs in various fractions of the biosphere e.g. the storage of carbon for a considerable period as 'living' wood as opposed to the annual production and decay of foliage. Similarly for the mean cycling time of carbon through the total biomass/

Figure 34. Transfer of Carbon between the Atmosphere and Biomass



biomass viz. 21 years, the presence of soil carbon fractions with apparent radiocarbon ages in excess of 2000 years must be recognised [Campbell 1965, and Gunning 1970].

(b) Computation of biogenic ^{14}C concentrations:

In the assessment of current rates of transfer of 'bomb' ^{14}C into the biomass several factors have to be considered, (i) the meridional inhomogeneity in tropospheric ^{14}C concentrations, (ii) the non uniform global distribution of the biomass, and (iii) seasonal variations in the photo synthetic activity of the bisophere. Clearly the coincidence of the maxima for seasonal variations in ^{14}C concentration and CO_2 fixation through photosynthesis has enhanced the transfer of 'bomb' ^{14}C to the biomass, particularly at northern latitudes.

Computations of the mean ^{14}C concentrations in the biomass were based on the series relationship,

$$\Delta Bn = \left[\frac{\Delta Tn + 20\ \Delta\ B(n - 1)}{21} \right]$$

where ΔBn is the mean ^{14}C concentration in the biomass in year 'n', ΔTn is the corresponding tropospheric ^{14}C concentration during the period of maximum photo-synthetic activity viz. July/August in the northern hemisphere/

hemisphere and November/December in the southern hemisphere, and the mean turn over time for biogenic carbon is 21 years. Individual ^{14}C concentrations were calculated for the northern and southern hemispheres and a weighted mean ^{14}C concentration for the total biomass was derived from these values. (The biogenic mass distribution between the northern and southern hemispheres was taken as 4.7×10^{17} gm C and 3.4×10^{17} gm C respectively [Junge et al. 1968].

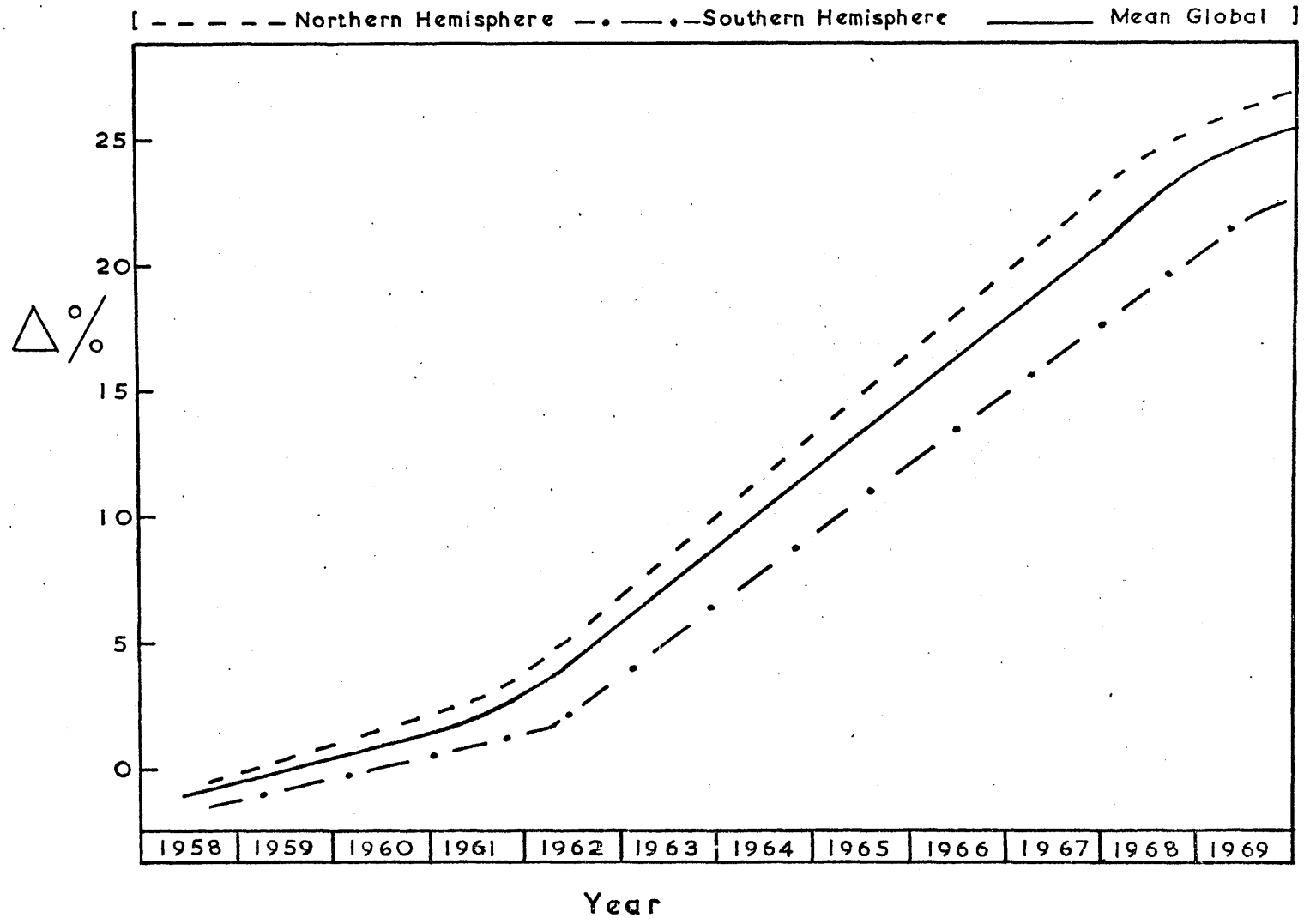
The results of these computations are presented in Fig. 35.

6.3. Conclusions

The tendency for concentrations of artificial ^{14}C in the atmosphere to decrease as atmospheric CO_2 exchanges with the biomass and oceans has been discussed previously. The condition of equilibrium distribution of ^{14}C between the atmosphere and biomass will not be attained, however, for several years. During the period required to establish this equilibrium the biomass accelerates the rate of decrease in atmospheric ^{14}C concentration.

The computed increase in biogenic ^{14}C concentrations between January 1964 and July 1968 is 12%. Since the relative mass distribution of carbon between the biomass and the atmosphere is 1.26 this corresponds/

Figure 35. Calculated Mean ^{14}C Concentrations in the Biomass



corresponds to a 15.2% decrease in the mean atmospheric ^{14}C concentration. An overall decrease of 62% in the ^{14}C concentration of the atmosphere is noted during this period. Thus the assimilation of ^{14}C by the biomass has been responsible for about one quarter of this reduction.

Clearly the rate of decline in the atmospheric burden of artificial ^{14}C will decrease when the biomass and the atmosphere attain equilibrium in ^{14}C concentration. Thereafter concentrations of ^{14}C in the atmosphere and biomass will be determined by the rate of exchange of CO_2 with the oceans, and the steadily increasing production rate of fossil fuel CO_2. The magnitude and future implications of these effects will be discussed in a subsequent chapter.

CHAPTER 7. ARTIFICIAL ^{14}C IN HUMANS.

7.1. Introduction

From the reported measurements of the distribution of 'bomb' ^{14}C in the dynamic carbon cycle it is possible to estimate the ^{14}C concentration in human tissue and to theorize on the potential hazards of this nuclide. Such theoretical computations have, in the past, assumed a simple correlation between human ^{14}C concentrations and those in the contemporary atmosphere or biosphere [Pauling 1958, Totter et al. 1958, and Purdom 1962]. Unfortunately the number of direct measurements of ^{14}C in human tissue is small. The data are sufficient to indicate, however, that the temporal variations of 'bomb' ^{14}C concentrations in certain population groups have differed significantly from those of the contemporary local environment. It appears that the discrepancies arose from the assumption that homogeneity in the distribution of 'bomb' ^{14}C in the atmosphere or atmospheric/biospheric reservoirs was attained rapidly.

(a) Review of published human ^{14}C concentrations:

The data of Broecker [1959], Libby [1964], Nydal [1963 and 1965], Berger et al. [1967], and L'Orange et al. [1968], demonstrated that the ^{14}C concentrations in human tissue were less than those monitored in the contemporary local atmosphere. Further, the concentrations of ^{14}C in/

in the skeleton were generally lower than those in soft tissue.

The results of Broecker [1959] and Libby [1964] were obtained during a period of steady increase in tropospheric ^{14}C concentrations, and to explain the observed deviations the authors introduced the concept of a 'lag time' between corresponding tropospheric and human ^{14}C concentrations. The apparent lag of 1 to 2 years in human ^{14}C concentrations was attributed to, (i) the time between photosynthesis and human consumption of food, and (ii) the finite residence time for carbon in human tissue. Although both are valid considerations their interpretation as a 'lag time' may well be misleading since this approach implies that in time human ^{14}C concentrations would rise to maximum values equal to those attained by the troposphere. Data reported by Berger et al. [1967], however, indicate a maximum Δ value of approximately 60‰ in human ^{14}C concentrations in the Western U.S.A. during 1965, whereas maximum tropospheric concentrations for this region were 95‰ (Δ) and these occurred during 1963 and 1964.

The low concentrations of ^{14}C in bone relative to soft tissue [Berger et al. 1967 and L'Orange et al. 1968] show a correlation with age. At a given time the mean/

mean ^{14}C concentrations in both the collagen and mineral fractions of bone decreased as a function of age. These variations suggest a longer residence time for carbon in bone than in soft tissue and also a decrease in the rate of renewal of the skeletal structure with age.

(b) The transfer of ^{14}C to man: ^{14}C is incorporated into human tissue via the food chain. The major source of carbon in the dietary intake originates in the photosynthetic fixation of atmospheric CO_2 by plants. Holt [1969] has estimated the average protein diet in Western Europe as 51% vegetable, 44% animal, and 5% fish. The finite and varied times for the transfer of ^{14}C through these branches of the food chain may well cause significant differences between the mean concentration of ^{14}C in the human diet and that of the contemporary atmosphere.

A wide range of plant materials have been investigated for their ^{14}C concentrations [Nydal 1965, Tauber 1967, Scharpenseel et al. 1968 and 1969, and Baxter 1969] and the results show an excellent correlation with contemporary tropospheric ^{14}C concentrations. Thus the transfer of ^{14}C from the atmosphere to the terrestrial food chain must be very rapid. The preservation and storage of vegetable food products and the residence time for carbon in animal tissue may be significant, however/

however, during the periods of rapid increase in atmospheric ^{14}C concentration. Importation of food from latitudes of different (generally lower) tropospheric ^{14}C concentration would also influence the mean dietary ^{14}C concentrations in the United Kingdom.

Concentrations of 'bomb' ^{14}C in the oceans have been considerably less than those in the atmosphere during the past decade. CO_2 collected from the euphotic zone of the oceans shows a slow increase in ^{14}C concentration with time reaching values of approximately +15‰ (Δ) during 1969 [Münnich et al. 1967 and Nydal et al. 1970]. It is to be expected, therefore, that marine food products will reflect these low ^{14}C concentrations and thus cause an additional reduction in the mean ^{14}C concentration of the human diet.

(c) Purpose of present study: In view of the uncertainties regarding the occurrence of 'bomb' ^{14}C in man further investigation of the concentrations of this isotope in human tissue and diets appeared necessary. Since the marked variations in tropospheric ^{14}C concentrations at United Kingdom latitudes during the past decade have been well documented, measurement of the corresponding concentrations in humans afforded a unique/

unique opportunity to investigate the transfer of carbon between man and his environment. The possible value of 'bomb' ^{14}C as a tracer for metabolic processes viz., the replacement rate of carbon in various tissues, could also be assessed from these observations.

7.2. Results

(a) ^{14}C concentrations in human tissue: The availability of blood plasma samples collected at recorded dates during the period 1952 to the present time enabled the documentation of human ^{14}C concentrations in the United Kingdom since the beginning of the nuclear era (Table 14). Each sample represented the combined plasma separated from the whole blood of 10 donors resident in southern Scotland, and in all cases the blood collection date was known to within $\pm$ 15 days.

The distribution of ^{14}C in the human body (Table 15) was investigated using samples obtained from a 37 year old female inhabitant of Glasgow who died of coronary artery disease during September 1969.

Since the health hazard from ^{14}C is primarily genetic the ^{14}C concentration in a composite sample of testes collected in southern England during 1969 was also measured (Table 15).

(b) ^{14}C concentrations in the human diet: A series of locally produced food products was monitored during/

TABLE 14. ^{14}C Concentrations Measured in Human Blood Protein.

BLOOD COLLECTION DATE		$\delta^{14}C\%$ $\pm 1\sigma$	$\delta^{13}C^{o}/oo$	$\Delta\%$ $\pm 1\sigma$
October	1952	- 3.6 ± 0.5	-28.4	- 2.9 ± 0.6
September	1953	- 8.1 ± 0.6	-26.4	- 7.9 ± 0.6
October	1953	- 2.9 ± 0.6	-27.7	- 2.3 ± 0.7
April	1954	- 5.5 ± 0.7	-26.2	- 5.1 ± 0.8
May	1954	- 1.5 ± 0.6	-29.4	- 1.4 ± 0.7
March	1955	- 1.6 ± 0.5	-26.2	- 1.3 ± 0.5
December	1955	- 1.2 ± 0.5	-26.2	- 0.9 ± 0.6
May	1956	- 7.8 ± 0.6	-29.5	- 7.0 ± 0.7
September	1957	- 5.0 ± 0.7	-30.8	- 3.9 ± 0.8
June	1958	- 2.0 ± 0.6	-28.5	- 1.3 ± 0.6
February	1960	9.0 ± 0.6	-26.5	9.4 ± 0.7
May	1961	16.4 ± 0.9	-27.2	16.9 ± 1.0
April	1962	9.9 ± 0.9	-29.4	10.8 ± 0.9
July	1963	32.0 ± 1.0	-32.3	33.9 ± 1.1
February	1964	44.4 ± 0.9	-29.4	45.6 ± 1.0
March	1965	60.1 ± 0.8	-29.5	61.5 ± 0.8
October	1966	65.4 ± 0.8	-27.2	66.2 ± 0.8
November	1966	64.0 ± 0.7	-30.0	65.6 ± 0.8
December	1966	64.5 ± 0.7	-27.9	65.4 ± 0.7
April	1967	64.2 ± 0.6	-28.4	65.3 ± 0.7
October	1967	62.6 ± 0.7	-33.2	65.3 ± 0.8
July	1968	63.2 ± 0.9	-26.3	63.4 ± 1.0
June	1969	52.4 ± 0.7	-31.5	54.4 ± 0.8

TABLE 15. Distribution of ^{14}C in the Human Body.

TISSUE	$\delta^{14}C\%$ ± 1σ	$\delta^{13}C°/oo$	$\Delta\%$ ± 1σ
Brain	58.3 ± 0.7	- 22.4	57.5 ± 0.8
Liver	50.3 ± 0.8	- 27.9	51.2 ± 0.8
Kidney	52.9 ± 0.7	- 20.5	51.5 ± 0.8
Uterus	45.9 ± 0.7	- 27.4	46.7 ± 0.7
Ovaries	53.5 ± 1.3	- 28.2	54.5 ± 1.4
Muscle	55.5 ± 0.7	- 26.6	56.0 ± 0.8
Fat	48.2 ± 0.8	- 30.4	49.8 ± 0.8
Bone Marrow	41.3 ± 0.8	- 34.2	43.9 ± 0.8
Bone Collagen	25.7 ± 0.7	- 27.6	26.4 ± 0.8
Bone Mineral	22.4 ± 0.7	- 17.1	20.5 ± 0.8
Testes	46.1 ± 0.7	- 29.3	47.3 ± 0.8

during 1967 through 1969 to allow a direct comparison with ^{14}C concentrations in the atmosphere and in human tissue. Since a correlation between ^{14}C concentrations in plant materials and in tropospheric CO_2 was already established the emphasis during this study was placed on food from animal and marine sources.

Concentrations of ^{14}C measured in terrestrial food products are presented in Table 16. ^{14}C concentrations monitored in a series of zooplankton and fish samples collected from the North Sea fishing grounds are presented in Table 17.

7.3. Implications of Results.

(a) General considerations: The data measured during this study indicate that human ^{14}C concentrations in the United Kingdom have been comparable with those reported for other population groups in Europe and North America. Maximum ^{14}C concentrations of 65‰ (Δ) in blood protein occurred during 1966-67 and these were approximately 30‰ (Δ) less than the peak tropospheric concentrations recorded 3 years earlier. Good agreement between contemporary blood protein and tropospheric ^{14}C concentrations was not achieved until late 1969. A relatively uniform concentration of ^{14}C throughout soft body tissue and blood protein was evident during 1969. In the skeleton of the same subject, however,

^{14}C/

TABLE 16. ^{14}C Concentrations in Food Produced in the United Kingdom.

SAMPLE DESCRIPTION	COLLECTION DATE		$\delta^{14}C\%$ $\pm 1\sigma$	$\delta^{13}C°/oo$	$\Delta\%$ $\pm 1\sigma$
Milk	July	1967	62.9±0.8	-23.7	62.4±0.9
Milk	September	1967	60.9±0.8	-24.2	60.8±0.8
Beef	August	1967	59.2±0.7	-27.2	59.7±0.8
Milk	August	1968	55.3±1.2	-23.7	54.9±1.2
Potatoes	September	1968	55.4±1.1	-23.6	54.9±1.1
Beef	August	1968	56.8±0.8	-26.0	57.0±0.9
Cheese	July	1969	52.6±1.2	-24.0	52.5±1.3
Beef	November	1969	54.1±0.7	-33.1	56.5±0.8

TABLE 17. ^{14}C Concentrations in the Marine Biosphere.

SAMPLE DESCRIPTION	LOCATION OF COLLECTION	$\delta^{14}C‰ \pm 1\sigma$	$\delta^{13}C°/oo$	$-\Delta‰ \pm 1\sigma$
Zooplankton	61°03'N.02°46'E.	7.4 ± 0.6	- 31.6	8.8 ± 0.7
"	61°03'N.02°46'E.	7.6 ± 0.6	- 27.2	8.2 ± 0.6
"	60°30'N. 0°30'W.	4.4 ± 0.6	- 29.0	5.2 ± 0.7
"	59°15'N.01°45'E.	9.5 ± 1.0	- 27.2	10.0 ± 1.0
"	58° 0'N.03° 0'E.	5.8 ± 1.0	- 36.8	8.3 ± 1.1
"	57°25'N.07° 0'E.	11.3 ± 1.0	- 27.0	11.8 ± 1.1
"	57° 0'N. 0° 0'E.	2.6 ± 0.7	- 34.2	4.4 ± 0.8
Cod Muscle	57°10'N. 1°50'W.	7.0 ± 0.4	- 24.4	6.8 ± 0.5
Whiting "	" "	10.8 ± 0.6	- 22.1	10.2 ± 0.7
Skate "	" "	1.6 ± 0.5	- 23.5	1.3 ± 0.6

Fish samples were collected during December 1968, zooplankton samples during May 1969.

^{14}C concentrations were considerably less than those measured in soft tissue and blood protein.

^{14}C concentrations measured in terrestrial food products indicated good agreement with contemporary tropospheric concentrations. The time involved in the transfer of ^{14}C to man by the assimilation of fresh vegetable and animal products is, therefore, short. However, the modification of the mean dietary intake of ^{14}C by the assimilation of preserved and imported food remains. On the other hand, the suspected low ^{14}C concentrations in marine food products is confirmed. It is interesting to note that the measured values are somewhat lower than would be expected from reported ^{14}C concentrations in oceanic CO_2 and it is possible that this reflects the presence of older carbon from the upwelling of deep water which is known to occur in the north Atlantic.

(b) <u>An assessment of the transfer of environmental carbon to man</u>: It is important for any future theoretical study to establish a relationship which explains the measured discrepancies between the concentrations of ^{14}C in man and those of his contemporary local environment.

If man is considered as an integral part of the terrestrial biosphere the relationship,

$$\Delta_{Bn} = \frac{\Delta_{Tn} + 2\Delta_{B(n-1)}}{3}$$

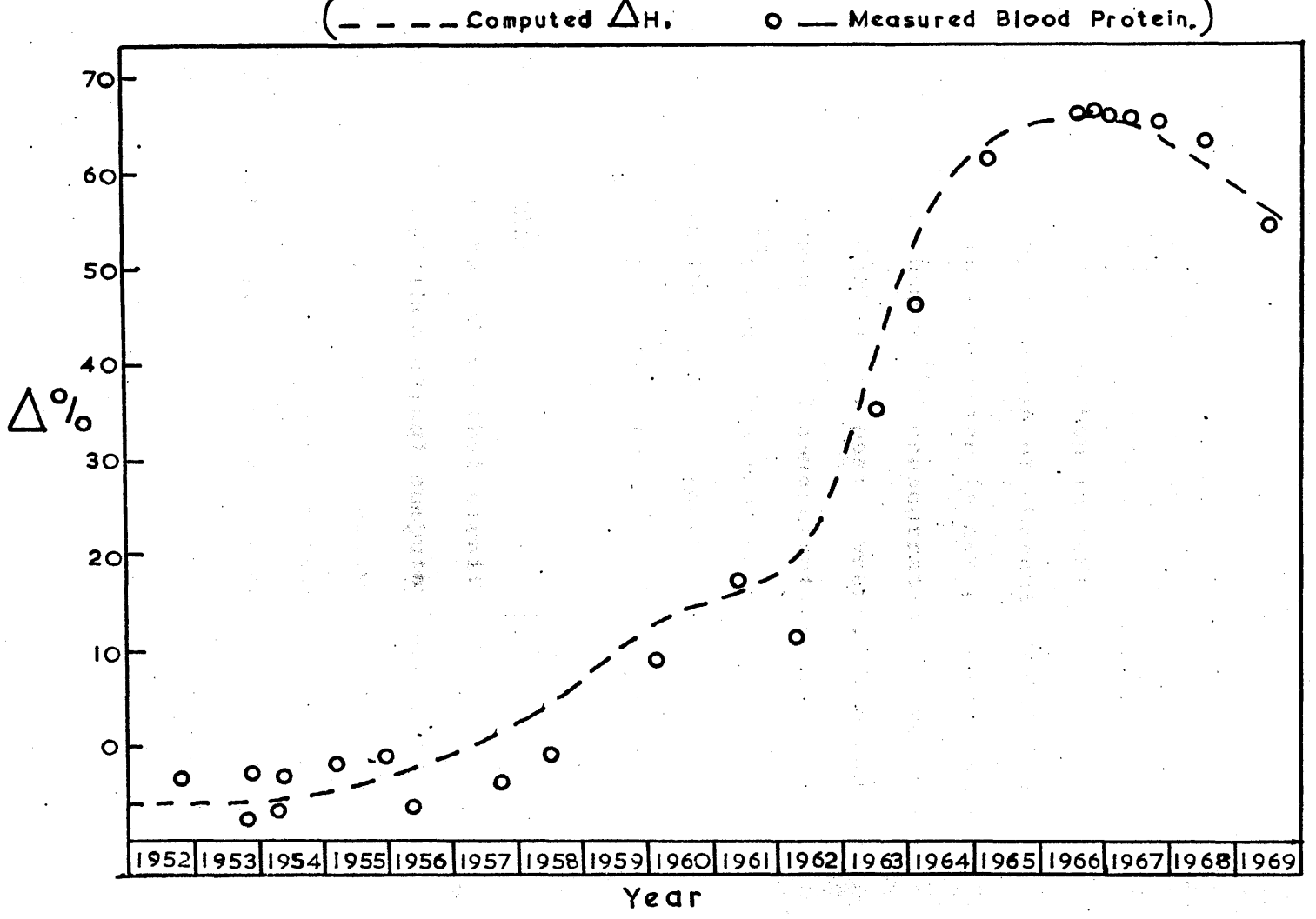
as derived in Chapter 6, should suffice. The concentration of ^{14}C in humans is, however, also dependent on the dietary carbon derived from marine sources (approximately 5%). Thus the expression,

$$\Delta_{Hn} = 0.95\ \Delta_{Bn} + 0.05\ \Delta_{On}$$

where Δ_H and Δ_O are the respective ^{14}C concentrations in human soft tissue and the ocean surface layer in year n, was considered more accurate. The results of this method of calculation and the comparison with observed ^{14}C concentrations in blood protein are shown in Fig. 36. The good agreement between the theoretical function and the observed variations in blood protein ^{14}C concentrations would indicate that the proposed method of computation of Δ_H lies within the uncertainties associated with direct measurement of the ^{14}C concentrations in human soft tissue.

(c) Rate of renewal of body carbon: Variations in the ^{14}C concentrations in the adult were most marked between soft tissue and skeletal carbon and this situation can only result from the carbon in bone structures being several years older than that in the remainder of the body. Slight variations in the ^{14}C concentrations of various soft tissues are also evident. With the limited number of data available, however, it is impossible/

Figure 36. Correlation Between Computed Human ^{14}C Concentrations and Observed Blood Protein Values.



impossible to determine whether these variations are real or within the limits of sampling error (the error quoted applies only to the uncertainty associated with ^{14}C measurement).

Broecker [1959] has estimated a mean residence time of a few months for carbon in soft tissue. Unfortunately the application of current 'bomb' ^{14}C concentrations to this question is not possible at the present time since human ^{14}C concentrations have passed through a maximum during the past 3 years. The conditions of uniform environmental ^{14}C concentration and a steady decline in human ^{14}C concentrations which should be established within the next few years would appear to provide an ideal opportunity for further studies of this nature.

7.4. Conclusions.

This study has shown that significant error may be involved in past theoretical computations which have accepted human ^{14}C concentrations estimated from model approaches. These errors are restricted, however, to the decade immediately following a period of artificial ^{14}C production, and arise mainly from the ill-defined function of the biosphere in relation to the dynamic carbon cycle.

In considerations of the total genetic hazard from/

from 'bomb' ^{14}C these errors are probably negligible since it appears that less than a few per cent of the total burden is delivered during the first 10 years after ^{14}C production. The magnitude of the error has significance, however, in assessments of possible somatic effects caused by ^{14}C in the generation which coincides with a period of artificial ^{14}C production.

The subject most susceptible to the discrepancies discussed involves the assessment of carbon transfer within the biosphere viz., food chain or human tissue exchange studies.

CHAPTER 8. FUTURE CONCENTRATIONS OF ARTIFICIAL ^{14}C IN THE ATMOSPHERE AND BIOSPHERE

8.1. Introduction

The ultimate disappearance of 'bomb' ^{14}C from the dynamic carbon cycle can only occur slowly in accordance with the 8268 ± 58 year mean life ($\tau = \frac{1}{\lambda}$) of this isotope. The present concentration of ^{14}C in the atmosphere and biosphere will decrease much more rapidly, however, as ^{14}C is transferred to the oceans during the next several decades. Libby [1955] has shown that, on average, a ^{14}C atom completes several passages through the dynamic cycle prior to decay and it is to be expected, therefore, that future atmospheric/biospheric ^{14}C concentrations will show two distinct phases viz., (i) a period of relatively rapid decrease due to the equilibration of excess ^{14}C within the carbon cycle, and (ii) a subsequent slow decline (with a half life of 5730 ± 40 years) in this quasi-equilibrium situation.

To date $7 \pm 2 \times 10^{28}$ artificial ^{14}C atoms have been produced during nuclear weapons' tests, [United Nations 1964] and in the absence of further major tests this would result in quasi-equilibrium ^{14}C concentrations 3% to 5% higher than the natural ^{14}C levels. The transient/

transient conditions which will exist during the interval necessary to establish this situation are dependent on the rates of mass transfer between the various carbon reservoirs. As discussed in Chapter 1, however, considerable disagreement exists in the exchange values reported in past studies and consequently the equilibration period is uncertain (in the range 20 to 200 years).

In considerations of present and future ^{14}C concentrations the 'Suess' effect, which has been disregarded in past computations, becomes increasingly important. Baxter [1969] has predicted an exponential rise in the magnitude of the 'Suess' effect such that the present 5% to 6% dilution in atmospheric ^{14}C concentrations will have increased threefold by the end of this century. It seems probable, therefore, that the release of fossil CO_2 will have countered artificial ^{14}C concentrations in the atmosphere and biosphere within the next 50 years.

In this study a reappraisal of the rates of carbon transport together with an estimate of the future release of fossil CO_2 to the atmosphere have been used to predict the temporal variations in atmospheric ^{14}C concentrations during the remainder of this century. These computations appeared important with/

with regard to, (i) compilations of the total radiation hazard from 'bomb' produced ^{14}C, and (ii) the possible continued application of artificial ^{14}C as a tracer in various natural processes.

8.2. Equilibration Rate of Artificial ^{14}C.

(a) Calculation of carbon exchange rates: From the temporal changes in the specific activity of 'bomb' ^{14}C measured in various carbon reservoirs it is possible to construct mathematical models which describe the dynamics of carbon transport [Plesset et al. 1960]. In these models it is assumed that the steady state conditions for stable carbon determine the rate of exchange for ^{14}C between the reservoirs of the carbon cycle. The exchange rate constant (k_{ij}) is then defined by the equation,

$$N_t = N_0 e^{-k_{ij}t} \quad \ldots\ldots (1),$$

which describes the decrease with time of the number of 'tracer' ^{14}C atoms (N_t) in one reservoir (i) through transfer to an adjacent reservoir (j) according to first-order kinetics. Nydal [1967] has defined the mean residence time (τ) for a carbon atom in a particular reservoir as,

$$= {}^{1}/_{N_0} \int_{t=0}^{\infty} N dt. \quad \ldots\ldots (2),$$

and/

and thus from equations (1) and (2), $\tau_i = {}^1/k_{ij} + {}^1/k_{il} + {}^1/k_{in}$ .... etc., where reservoir (i) has a common interface with reservoirs, j, l, n, ... etc.

As discussed previously, any evaluation of the exchange rate constants is subject to uncertainties imposed by differences between the model and the real system. Thus early studies required complex models to describe the marked disequilibrium in 'bomb' ^{14}C distribution at that time, and the disagreement in exchange values obtained from these computations is probably a result of model limitations allied with uncertainties in the data available for model construction. Fortunately the tendency for ^{14}C concentrations in the atmosphere and biomass to become more uniform with time has reduced the requirement for complex models. Together with the additional data available from continued investigations of ^{14}C distribution, more confidence can now be placed in exchange rate calculations. Limitations remain, however, even at the present time, the most significant being (i) the ill-defined size and function of the biomass, and (ii) the limited data available for ^{14}C concentrations in the oceans.

A reappraisal of carbon exchange rate constants (Table 18)/

(Table 18) was made from the application of a series of box model treatments to the transient distribution of excess ^{14}C during 1967 through 1969, and as discussed in previous Chapters [Walton et al. 1970].

The values determined in this re-examination fell within the range of previous estimates although the computed mean residence time for carbon in the oceans (approximately 500 years) is somewhat less than most earlier values. A significant feature emerging from this study was the short term buffering effect of the biomass for tropospheric ^{14}C concentrations. Thus during the past decade the decrease in tropospheric ^{14}C concentrations has been accelerated by the net uptake and retention of ^{14}C in biogenic structures. In future years, however, the biomass will lengthen the 'apparent' mean residence time for ^{14}C in the troposphere through the return of ^{14}C atoms to this reservoir.

(b) Computation of the future distribution of ^{14}C:

Prediction of the transfer of excess ^{14}C from the atmosphere and biosphere must be based on an extrapolation of the models employed for the determination of carbon exchange constants. The question arises as to how representative a particular model is for this purpose bearing in mind the quality of the data available for its construction. Investigations reported earlier in this/

TABLE 18. Exchange Rate Constants in the Dynamic Carbon Cycle.

RESERVOIR EXCHANGE	SUBSCRIPT (ij)	EXCHANGE RATE CONSTANT (k_{ij}), $years^{-1}$
Stratosphere to Troposphere	st	0.250
Troposphere to Biomass	tb	0.148
Troposphere to Surface Ocean	tm	0.108
Surface Ocean to Troposphere	mt	0.073
Surface Ocean to Deep Ocean	md	0.090
Deep Ocean to Surface Ocean	dm	0.002

this study suggest that the terrestrial carbon reservoirs viz., the stratosphere, troposphere, and biomass will attain uniform ^{14}C concentration (to within $\pm$ 5%) before 1975. The subsequent decrease in this ^{14}C concentration will then be determined by the rate at which atmospheric $^{14}CO_2$ enters the oceans, and the approximate 500 year mean residence time for oceanic carbon.

A relatively simple two box model (Fig. 37) is probably adequate to describe this situation. The mathematical treatment of this model is as follows:

Let, N_0 = the amount of ^{14}C in the terrestrial reservoir at time t_0,

N_1 = the amount of ^{14}C retained in the terrestrial reservoir at time t(years),

N_2 = the amount of ^{14}C transferred to the oceans after time t(years),

k_1 = the exchange constant for the transfer of carbon from the terrestrial to the oceanic reservoir,

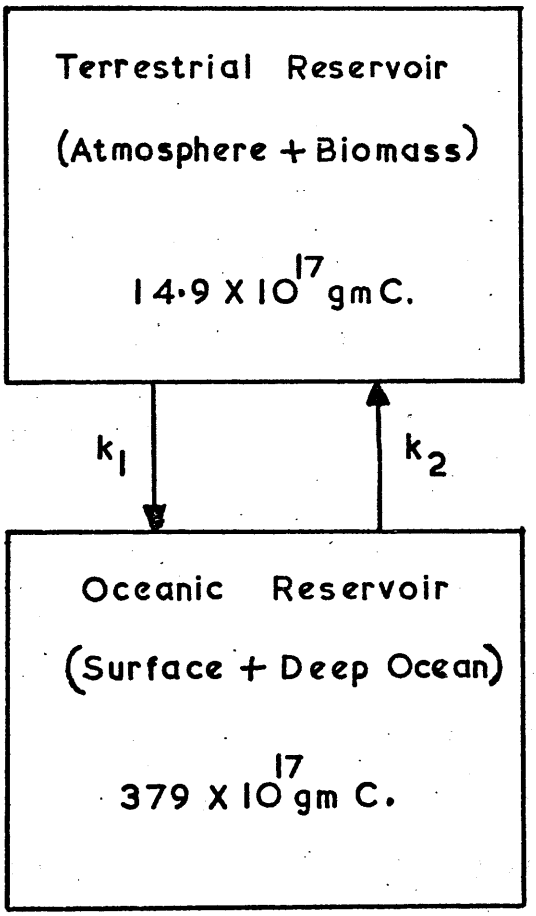
k_2 = the exchange constant for the transfer of carbon from the oceanic to the terrestrial reservoir,

and λ = the disintegration constant for ^{14}C (0.000121 $year^{-1}$).

The transient distribution of ^{14}C in the system

is/

Figure 37. Model for the Prediction of Future Atmospheric/Biospheric ^{14}C Concentrations.



is then described by the equations,

$$dN_1/dt = -k_1N_1 + k_2N_2 - \lambda N_1 ,$$

and

$$N_1 + N_2 = N_0e^{-\lambda t}$$

The solution for N_1 has the form,

$$N_1 = N_0\left[\frac{k_1}{k_1+k_2} e^{-(k_1+k_2+\lambda)t} + \frac{k_2}{k_1+k_2} e^{-\lambda t}\right]$$

Calculations based on this relationship require an evaluation of the k values for the simplified model in which the biomass, troposphere, and stratosphere are considered as a single unit. Since carbon retained in the biomass and the stratosphere is not available for exchange with the oceans the mean residence time for carbon in the combined terrestrial reservoir must be greater than the 9.3 years calculated for tropospheric CO_2 (Table 18). From the definition of the exchange rate constant the parameter/

parameter k_1 in the two box model is then,

$$= \frac{k_{tm} R_t}{R_t + R_s + R_b} = 0.048 \text{ year}^{-1} ,$$

where R_t, R_s, and R_b are the respective masses of carbon in the troposphere, stratosphere, and biomass. Similarly carbon in the deep ocean is not available for direct transfer to the troposphere, therefore,

$$k_2 = \frac{k_{mt} R_m}{R_m + R_d} = 0.0019 \text{ year}^{-1} ,$$

where R_m and R_d are the respective masses of carbon in the surface and deep ocean layers.

For a uniform distribution of ^{14}C in the terrestrial carbon reservoirs the model parameters N_0 and N_1 are by definition synonymous with the contemporary Δ values of tropospheric CO_2. This homogeneous situation will not be finally attained, however, until 1975 and prior to this date a mean ^{14}C concentration for the terrestrial reservoir ($\bar{\Delta}$) /

($\bar{\Delta}$) must be applied in the model viz.,

$$\bar{\Delta} = \frac{R_s \Delta_s + R_t \Delta_t + R_b \Delta_b}{R_s + R_t + R_b}$$

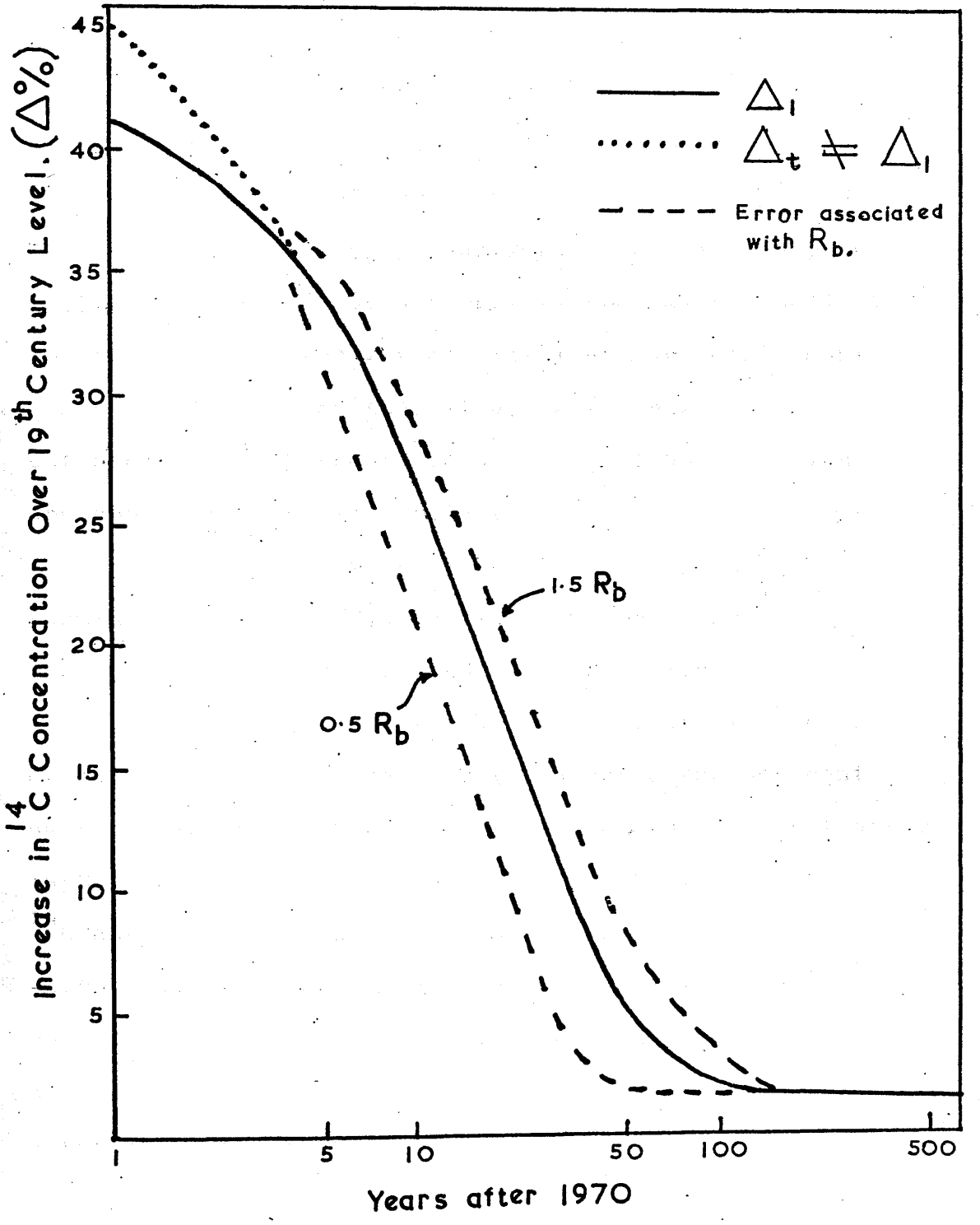
$\bar{\Delta}$ calculated for January 1970 was 43‰, and the future reduction of ^{14}C concentrations in the terrestrial reservoir due to exchange with the oceans (Fig. 38) was computed from the relationship,

$$\Delta_1 = \bar{\Delta}_{[1970]} (0.96e^{-0.05t} + 0.04e^{-0.000121t})$$

The present inhomogeneous distribution of ^{14}C in the terrestrial reservoir leads to a computed $\bar{\Delta}_{[1970]}$ value which is lower than the observed tropospheric/biospheric ^{14}C concentration (Δ_t = 48‰) at January 1970. However, this -5‰ error in model evaluations of Δ_t will decrease with time and approach zero by 1975.

The greatest uncertainty in this treatment is the variations in the exchange rate constants (k_1 and k_2) which will result from error in the assessment of the carbon content of the biomass. To indicate the extent of this uncertainty the variations in Δ_1 caused by a $\pm$ 50% error in the accepted inventory of biogenic carbon are included in Fig. 38.

Figure 38. Reduction of Terrestrial ^{14}C Concentrations through Equilibration with Oceanic Carbon



8.3. Contribution of the Suess Effect to Future Terrestrial ^{14}C Concentrations.

Prediction of the Suess effect must be speculative due to uncertainty in future fossil fuel consumption. It is to be expected that the introduction of alternative energy sources viz., nuclear power and solar radiation, and the exhaustion of coal and oil supplies will reduce the rate of fossil CO_2 production. According to Putnam [1954], however, these alternative sources are unlikely to exceed 20% of the world's total energy requirement before 2025 A.D. and thus it appeared reasonable to extrapolate the present trend in fossil CO_2 dilution to the end of the present century.

Walton and Baxter [1970], in a comprehensive examination of past fluctuations in atmospheric ^{14}C concentrations, have derived the expression $S_t = -3.1\ e^{0.034t}$ to describe the increase in the Suess effect between 1950 and 1969 (S_t denotes the per cent decrease in terrestrial ^{14}C concentration in year t after 1950). From this relationship the reduction in atmospheric ^{14}C concentration due to the Suess effect at 1969 was -6.0% (Δ), and the $\bar{\Delta}$ value applied in the exchange model included this dilution. The additional reduction of terrestrial ^{14}C concentrations from the Suess effect after 1969 was, therefore, derived from the relationship,

$$\Delta' = -3.1e^{0.034(t+19)} + 6.0,$$

where Δ' is the per cent decrease in ^{14}C concentration in year t after 1969.

The role of the predicted Suess effect (Δ') in the determination of future ^{14}C concentrations in the terrestrial carbon reservoirs ($\Delta_1 + \Delta'$) is shown in Fig. 39.

8.4. Conclusions.

As shown in Fig. 38 approximately 100 years will pass before artificial ^{14}C introduced into the upper atmosphere becomes uniformly distributed throughout the dynamic carbon cycle. A possible error of $\pm$ 50 years is involved in this computation due to present uncertainty of the amount of carbon held in the biogenic reservoir. In the determination of future concentrations of ^{14}C in the atmosphere and biosphere, however, the Suess effect is the predominant factor and should result in these concentrations being close to the natural 'prebomb' levels by the end of the present century.

Extension of the present treatment beyond 2000 A.D. does not appear feasible at the present time since apart from uncertainty as to the sources of energy after this date additional factors seem pertinent. The release of CO_2 to the atmosphere has disturbed the sensitive equilibrium processes of the carbon cycle. Basic thermo-

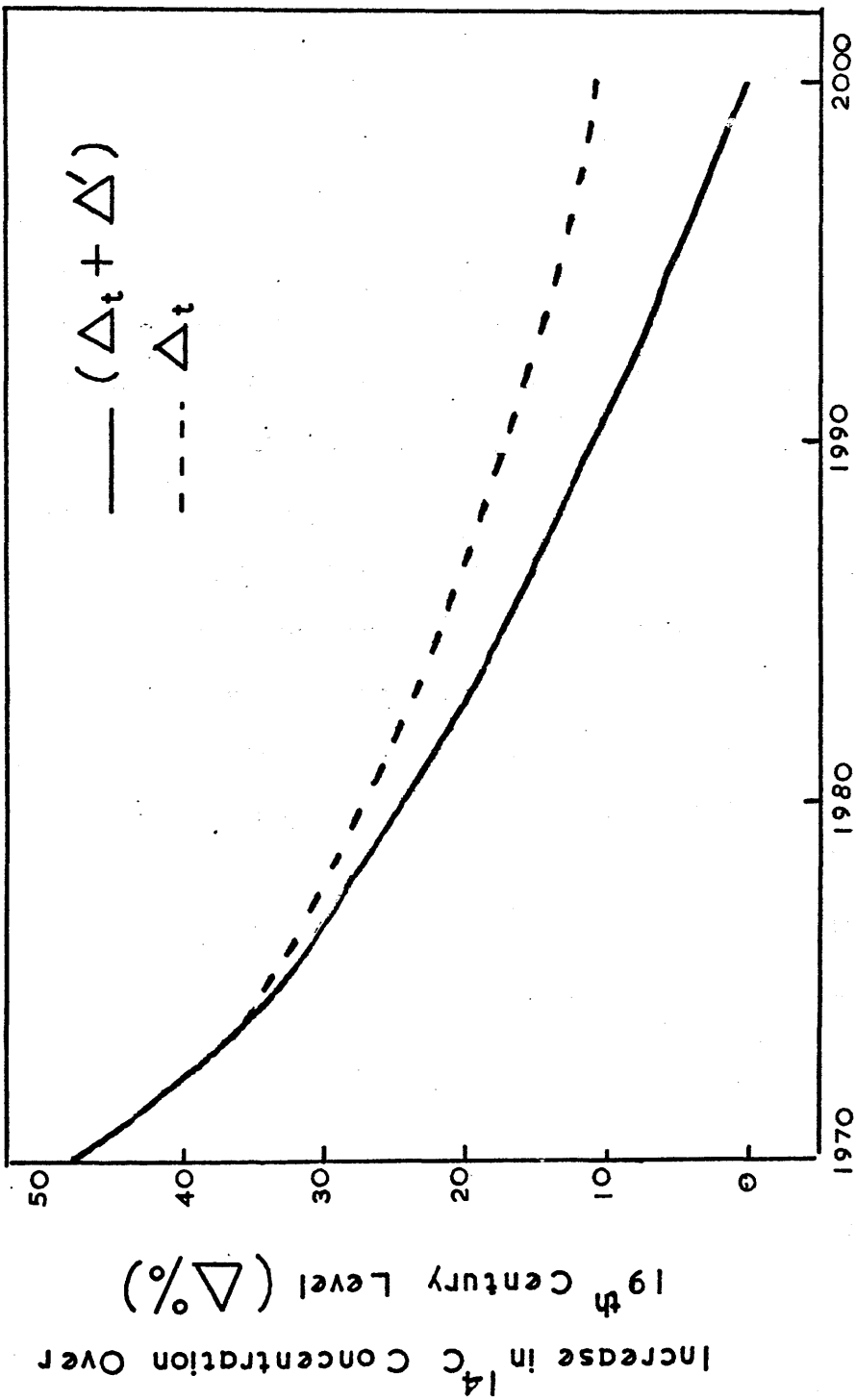


Figure 39. Predicted Terrestrial ^{14}C Concentrations 1970 to 2000 A.D.

dynamical considerations would indicate a net transfer of CO_2 from the atmosphere to the oceans to counteract this situation and thus the steady state conditions implied in our model evaluations are not strictly valid. At the present time the increase in atmospheric CO_2 content from fossil fuel consumption is approximately 10% [Bischof et al. 1966]. If it is assumed that the transfer rates for CO_2 exchange between the atmosphere and oceans are governed by Henry's Law then the present net transfer from the atmosphere is within the error involved in exchange rate constant computations. By 2025 A.D., however, the concentration of excess CO_2 in the atmosphere may have risen to 50%, in which case the present theoretical treatment will no longer apply.

The rate of transfer of CO_2 to the oceans is not, however, simply a function of the partial pressure of this gas in the atmosphere. According to Bolin et al. [1959] the large-scale transfer of CO_2 to the oceans will lower the pH and hence increase the dissociation of H_2CO_3 and CO_3^{2-} species resulting in a reduction of the atmosphere/ocean transfer rate. An increase in the earth's surface temperatures is also possible through enhanced absorption of infrared radiation by higher atmospheric CO_2 concentrations (the 'greenhouse' effect). This effect would also serve to increase the return flux of CO_2 from the oceans.

The imbalance in the natural distribution of carbon prepetrated by man's technological progress would appear to have serious implications for the future environment. Over the remainder of this century artificial ^{14}C will continue to serve as an excellent tracer for our further understanding of these environmental changes.

APPENDIX I

Regressional Analysis - Background Count Rate as a Function of Barometric Pressure

For a given counting period the measured count rates showed a linear relationship with barometric pressure. The relationship is given by the regression of the observed counting rate on barometric pressure since the latter values were assumed constant during any individual counting sequence, i.e.,

$$Y = a + bx$$

where Y = mean count rate (cpm), x = measured barometric pressure (mbar.), and b = regression coefficient.

The regression for a set of 'n' data each comprising a measured count rate (y), and the corresponding barometric pressure (x), was calculated on a K.D.F.9 digital computer using the following 'least squares fit' programme.

```
DA300171WPU+X330077HPSU→

begin  comment  This programme works out m and c for the
          equation y = mx + c by least squares from n
          pairs of x and y and gives the rms error
          (sqrt([v↑2]/(n - 2) ) plus thendividual
          deviations in y ;

integer  n, i, p;
real  sx, sy, sxy, sx2, sy2, m, c, d;
open(20);  open(70);



start:  n:= read(20);


begin  array  x,y, e [1:n];
sx:=sy:=sxy:=sx2:=sy2:=0.0;
for i:=1 step 1 until n do
begin  x[i]:= read(20);
       y[i]:= read(20)
end;
for i:=1 step 1 until n do
begin sx:= sx + x[i];
      sy:= sy + y[i];
      sxy:=sxy + x[i]×y[i];
      sy2 := sy2 + y[i]↑2;
      sx2:=sx2 + x[i]↑2
end;

d:= n×sx2 -sx↑2;   m:= (n × sxy -sx × sy)/d;
c:= (sx2 × sy - sx × sxy)/d;
d:= sqrt((sy2 - sy × c - sxy × m)/(n - 2));

for i:= 1 step 1 until n do
  begin

  e[i] := y[i];
  y[i] :=  y[i] - m × x[i] - c
  end;

write text (70, [[4c] m*=*]);
write (70, formats([-d.ddd[d10-nd]]), m);
write text (70, [[3s]c*=*]);
```

```
WRITE 870000000000000 format([-d.ddddd10-nd]), c);
write text (70, [[3s] rms*error*=*]);
write (70, format ([-d.ddddd10-nd]), d);
write text (70, [[3c][6s]v*obs[8s]y*calc [7s]deviation[2c]]);
for i := 1 step 1 until n do
  begin
    write (70, format ([2s -d.dddd10-nd]), e[i]);
    write (70, format ([3s -d.dddd10-nd]), m × x[i] + c);
    write (70, format ([3s -d.dddd10-ndc]), y[ii])
end;
comment  if another set of data is to follow punch 1 otherwise 0;

p := read (20);
if p = 1 then goto start;
close (70);
close (20);
comment The data tape consists of n followed by n pairs of
    values of x and y.  A 1 is punched after each set of n
    pairs if another set follows, and a zero after the
    final set;

end   end  →
```

Estimation of error on Y: since the variation about the functional relationship was assumed to be due solely to error in the observations of 'y', the variance about the final relationship is an estimate of the error variance of Y. The standard error estimate is less than that for any one experimentally determined 'y' due to the averaging out of individual observations in the process of fitting the line.

The standard error (S.E.) of the estimate obtained for a given value $x = x'$ is:

$$S.E.(Y') = S\sqrt{[1/n + (x' - \bar{x})^2/\Sigma (x - \bar{x})^2]}$$

where S = the variance about the line i.e. possible error on the slope.

$$S. = \sqrt{\frac{\Sigma (y - \bar{y})^2 - b^2 \Sigma (x - \bar{x})^2}{(n - 2)}}$$

N.B. The term (n - 2) arises from the two degrees of freedom applicable in this treatment.

APPENDIX II

Correction of the Measured Beta Activity for Rn Plus Daughter Contribution

It was evident from numerous counting sequences that a residual alpha count rate (0.05 cpm) existed within the detector. These pulses registered in energy channel 3 and were assumed to arise from traces of elements of the U and Th series in the counter materials. A similar effect, but to a greater degree was noted by Fergusson [1955].

A high alpha activity, decaying with a half life of 3.8 days, was noted in freshly prepared counting gas. This corresponds to ^{222}Rn impurity in the gas. In addition to the alpha pulses monitored, beta events from the daughter products of the ^{222}Rn decay scheme will be included in the lower energy channel counting rates.

To avoid wasted counting runs the relationship between ^{222}Rn alpha pulses and the equilibrium daughter beta emissions was determined by ^{222}Rn seeding of a CO_2 sample. The following correction was derived and applied to the measured count rates where necessary.

Let:

A = Sample activity (cpm) in the absence of Rn.

A' = total measured anticoincidence events (cpm)

i.e., $A/C_1 + A/C_2 + A/C_3$, where A/C_1, A/C_2 and A/C_3 are the count rates in the appropriate energy channels.

R/

R = Ratio of Rn + daughter activity between

$(A/C_1 + A/C_2)$ and A/C_3 i.e. $^{\beta}/_{\alpha}$ activity.

x = Residual alpha activity (0.05 cpm).

The total pulses due to Rn + daughters, when present are then (R + 1) = Y cpm.

From Rn seeding experiments under routine gas counting conditions R = 1.565 ± 0.025 (cpm) therefore

Y = 2.565 ± 0.025 (cpm)

Then $A = A' - [\, Y\,(A/C_3 - x)\,]$ cpm

The error on A, at the 2σ confidence level is given by:

$$\pm 2\sigma = \pm 2 \sqrt{Y.A/C_3 \left[\left(\frac{\sigma_{A/C_3}}{A/C_3} \right)^2 + \left(\frac{\sigma_Y}{y} \right)^2 \right]^{\frac{1}{2}} + (\sigma_{A'})^2}$$

The term $(\sigma_Y/Y)^2$ is negligible therefore the above equation simplifies to:

$$\pm 2\sigma = \pm 2 \sqrt{[Y.\sigma_{A/C_3} + (\sigma_A 1)^2\,]} \text{ cpm}$$

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CARBON-14 IN THE BIOSPHERE AND HUMANS

By
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Carbon-14 in the Biosphere and Humans

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Many methods have been used to calculate the quantity of carbon-14 reaching human bodies from the environment as a result of nuclear fission and fusion. Comparisons with measurements of carbon-14 in blood samples show that these calculations can be wrong, particularly during the first ten years after a sharp increase in environmental radiation.

THE radiation hazard to man arising from the ingestion of fission nuclides has received considerable attention during the past twenty years. Considerable effort and publicity have been focused on factors such as the deposition of ^{90}Sr and ^{137}Cs in bone, the occurrence of ^{131}I in thyroid tissue, and the inhalation dose from short lived nuclides such as ^{89}Sr, ^{95}Zr, ^{106}Ru, ^{140}Ba, ^{144}Ce, and so on. The potentially hazardous character of ^{14}C, although outlined early by Pauling[1], Totter *et al.*[2], and Leipunsky[3], has not attracted as much attention.

Numerous data have been reported on the distribution of "bomb ^{14}C" in the atmosphere and oceans which permits theoretical estimates to be made of human ^{14}C levels in the past, present and future. The volume of published data on measured concentrations of ^{14}C in human tissue for comparison with such estimated values is, however, extremely limited[4–7]. We have therefore reviewed some of the limitations in the estimates of human ^{14}C levels and compared the theoretical results with measured data from blood protein carbon.

Before the mid-nineteenth century there was a "steady state" distribution of cosmic ray produced ^{14}C within the carbon cycle. During the past century, however, two of man's activities have upset this situation. First, the combustion of fossil fuels has released large quantities of ^{14}C-free carbon dioxide to the atmosphere, resulting in a decrease of ^{14}C specific activity (Suess effect). Second, the testing of nuclear devices has added ^{14}C to the atmosphere resulting in a corresponding rise in the ^{14}C specific activity (bomb effect). The relative magnitude of these effects was such that by the mid-twentieth century the Suess effect had decreased the atmospheric ^{14}C activity by approximately 3 per cent, whereas the bomb ^{14}C produced during the period 1945 until 1962 was sufficient to increase the tropospheric ^{14}C level of the northern hemisphere to 100 per cent above natural concentrations in 1963. Thus it is possible to construct mathematical models of the mass transfer within the dynamic carbon cycle based on the changes in ^{14}C specific activity measured in the various reservoirs, and arising from either the Suess or the bomb effects. The construction and evaluation of such models have been discussed in detail by Plesset and Latter[8].

Estimating Human ^{14}C

Many mathematical models of varying complexity have been applied to the dynamics of carbon transfer. Any estimate of ^{14}C in mankind must be related to these models. The question arises as to how representative a particular model is for this purpose, bearing in mind the quality of the experimental data available for its construction. Possible limitations on the use of any theoretical treatment include the following. (1) Uncertainties in the values of the parameters which govern the transport of carbon dioxide within the carbon cycle, particularly with respect to the biosphere. (2) The basic assumption, made in any mathematical treatment, that the internal mixing time for carbon in a given reservoir is negligible in relation to the exchange time between adjacent reservoirs. (This is clearly not the case.) (3) The concept that the mass transfer flux across reservoir boundaries is uniform in location and time. (4) Concentrations of ^{14}C in man are likely to be quite different from those in the terrestrial biosphere for two reasons: (*a*) the nature of the human diet favours the assimilation of young terrestrial biospheric carbon, and (*b*) the diet usually includes carbon of marine origin with a lower concentration of ^{14}C.

Errors in estimates of human ^{14}C levels arise from the uncertainties in calculations of biospheric concentrations of ^{14}C at various times after a stratospheric injection of artificial ^{14}C. To illustrate this problem we have compared the predicted terrestrial biospheric ^{14}C levels from a simple two box model (Fig. 1) with those from a more complex six box model (Fig. 2) for all estimated bomb ^{14}C produced so far. The rates of production of ^{14}C (Table 1) are based on published fission and/or fusion energy yields and are calculated from the relationship, 2×10^{26} ^{14}C atoms per Mton for an air burst, and 1×10^{26} ^{14}C atoms per Mton for a surface burst. All ^{14}C is considered as being injected directly into the stratosphere. The experimental parameters used in the construction of each model (Tables 2 and 3) are calculated from recent measurements in this laboratory[9].

Comparisons of the predicted biospheric levels derived from each model are shown in Fig. 3. It is clear that the

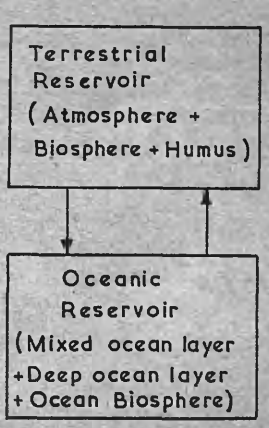

Fig. 1. Two box model for dynamic carbon cycle.

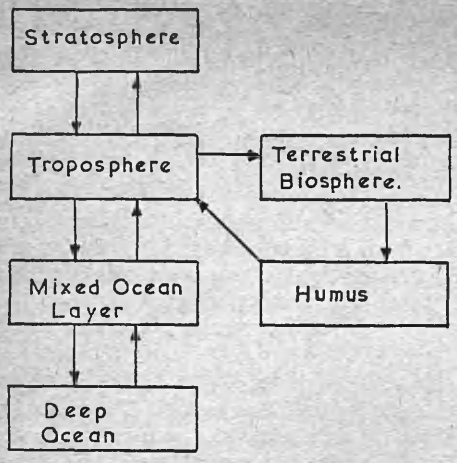

Fig. 2. Six box model for dynamic carbon cycle.

Table 2. DISTRIBUTION OF CARBON IN THE DYNAMIC CYCLE

Reservoir	Carbon mass (10^{17} g)
Stratosphere	1·05
Troposphere	5·52
Biosphere	1·24
Humus	7·10
Mixed ocean layer	8·16
Deep ocean layer	371·00

Table 3. EXCHANGE RATE CONSTANTS (k)* FOR CARBON IN THE DYNAMIC CYCLE

Exchange between reservoirs	k value (years^{-1})	Application
Terrestrial to oceanic	0·09	Two box model
Oceanic to terrestrial	0·0016	
Stratosphere to troposphere	0·25	Six box model
Troposphere to stratosphere	0·05	
Troposphere to biosphere	0·12	
Biosphere to humus	0·54	
Humus to troposphere	0·10	
Troposphere to mixed ocean	0·11	
Mixed ocean to troposphere	0·07	
Mixed ocean to deep ocean	0·09	
Deep ocean to mixed ocean	0·0020	

* Reciprocal of the mean residence time for carbon in a given reservoir prior to transfer.

simple treatment (two box model) is adequate for times 12 years after a major stratospheric injection of ^{14}C. Further, the error involved in assessments of human ^{14}C levels after this period is negligible, for the general limitations discussed previously will be inapplicable because of the virtual homogeneity of excess ^{14}C throughout terrestrial carbon reservoirs.

The major problem arises, however, in the computation of human ^{14}C levels during the decade immediately after a period of ^{14}C production. Probably the largest source of error in this period arises from uncertainties regarding the biosphere. To investigate this aspect further we have measured the variation in ^{14}C concentrations in human blood protein obtained from plasma collections from southern Scotland during the period 1952 until the present and compared the results with the predicted concentrations.

^{14}C in Blood

We obtained samples of dried human plasma contained in sealed flasks. Each sample represented the combined plasma separated from the whole blood of ten donors resident in southern Scotland (approximately 20 g of protein). In all cases the plasma separation date was known, and this corresponded to a blood collection date 30 ± 5 days previously. Small, but known, quantities of dextrose and sodium hydrogen citrate had been added to each sample during its preparation for storage, and this constituted carbon contamination so that pretreatment was carried out to recover the protein fraction. The plasma was reconstituted by the addition of water and the protein was precipitated using trichloroacetic acid. The protein was recovered by filtration, and washed free from dextrose, citrate and acetate, using dilute hydrochloric acid followed by water. This pretreatment resulted in better than 90 per cent recovery of pure protein. The protein carbon was converted to carbon dioxide by combustion in a stream of oxygen and the gas was purified for later ^{14}C measurement in a carbon dioxide anti-coincidence proportional counting system. We used a 2·6 litre counter filled to one atmosphere pressure. In these conditions the background counting rate is 5 c.p.m., and the net rate for standard gas prepared from National Bureau of Standards oxalic acid is 15 c.p.m. The activity of each sample was measured for at least two independent counter fills, and a minimum total of 60,000 counts was recorded. The isotopic fractionation for ^{13}C in each sample gas was measured relative to the Peedee Belemnite Chicago Limestone Standard, and the measured ^{14}C enrichment was corrected accordingly. Results are quoted in Table 4, as percentage enrichment over the standard using the method described by Broecker and Olson[10].

The measured values (Table 4) can be compared with the predicted biospheric levels from the box models (Fig. 3). The discrepancies shown are a measure of the combined error from the general limitations imposed by a box model treatment as discussed previously and that involved in relating ^{14}C production to published nuclear energy yields.

Measurement of ^{14}C in ground level air collected from a worldwide sampling network[9] shows that uniformity of bomb ^{14}C concentration (to within ± 5 per cent) was

Table 1. ESTIMATED "BOMB ^{14}C" PRODUCTION SO FAR

Period	^{14}C yield (10^{27} atoms)	Mean annual production (10^{27} atoms)
1945–51	0·1	0·015
1952–54	6·0	2·0
1955–56	3·9	1·95
1957–58	14·2	7·10
1959–60	Nil	Nil
1961	24·0	24·0
1962	43·4	43·4
1963	Nil	Nil
1964–66	0·02	0·005
1967	1·0	1·0
1968	2·0	2·0

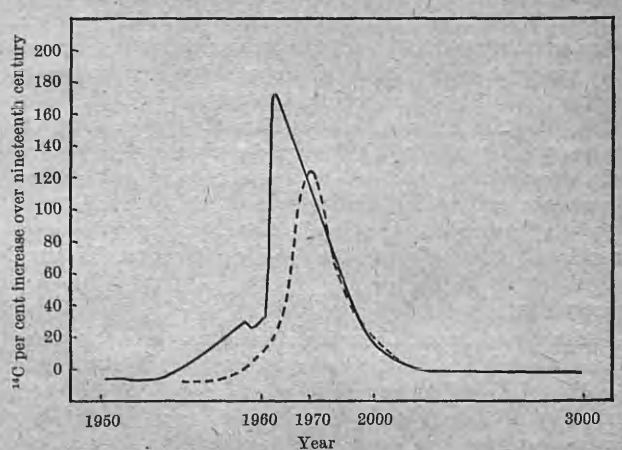

Fig. 3. Terrestrial biospheric ^{14}C levels estimated from energy yield data. ——, Two box model; – – –, six box model.

Table 4. $^{14}C/^{12}C$ RATIOS MEASURED IN HUMAN BLOOD PROTEIN

Blood collection date	$\delta^{14}C\% \pm 1\sigma$	$\delta^{13}C^0/_{00}$	$\Delta\% \pm 1\sigma$
26.10.52	−3·61 ± 0·5	−28·43	−2·94 ± 0·6
23.3.55	−1·60 ± 0·5	−26·17	−1·31 ± 0·5
5.5.56	−7·84 ± 0·6	−29·45	−7·02 ± 0·7
26.9.57	−5·04 ± 0·7	−30·77	−3·94 ± 0·8
23.5.61	16·42 ± 0·9	−27·18	16·92 ± 1·0
7.4.62	9·85 ± 0·8	−29·36	10·81 ± 0·9
15.7.63	31·97 ± 1·0	−32·27	33·89 ± 1·1
9.2.64	44·36 ± 0·9	−29·42	45·63 ± 1·0
5.3.65	60·06 ± 0·8	−29·51	61·51 ± 0·8
17.10.66	65·44 ± 0·8	−27·18	66·16 ± 0·8
15.11.66	63·97 ± 0·7	−30·01	65·62 ± 0·8
30.12.66	64·47 ± 0·7	−27·86	65·41 ± 0·7
8.4.67	64·19 ± 0·6	−28·44	65·32 ± 0·7
27.10.67	62·64 ± 0·7	−33·21	65·31 ± 0·8
10.7.68	63·23 ± 0·9	−26·33	63·40 ± 1·0

obtained throughout the troposphere only during late 1968. Because the human ^{14}C concentration is primarily governed by the photosynthetic fixation of tropospheric ^{14}C, a corresponding worldwide variation in human ^{14}C levels will be evident before this date. This fact is not accounted for in either box model treatment.

To minimize the limitations of the box model approach due to the finite time required for atmospheric mixing and the error involved in calculation of the ^{14}C production inventory, we have compared the measured blood protein ^{14}C data with the well documented tropospheric ^{14}C activities in the latitude band 50°–60° N. We have also predicted the corresponding terrestrial biospheric ^{14}C levels using these values (Fig. 4). Thus in effect we have investigated the relationship between ^{14}C concentrations in man and those in his contemporary local environment.

Estimating the Biospheric ^{14}C

The calculation of a representative value for ^{14}C enrichment in the terrestrial biospheric reservoir must be speculative because of its diverse physical composition and uncertainty regarding the masses of carbon involved. In this treatment we have chosen the basic data and the approaches of Lieth[11] and of Junge and Czeplak[12]. Because the mass of biospheric carbon is $1{\cdot}24 \times 10^{17}$ g, and the annual fixation of biospheric carbon is $0{\cdot}384 \times 10^{17}$ g, a mean turnover time for biospheric carbon is approximately three years. On this assumption the biospheric enrichment value (ΔB per cent) at the beginning of any year n was calculated using the relationship

$$\Delta B = \frac{\Sigma_{(n-1)}^{(n-3)} \Delta T}{3} \qquad (1)$$

where Δ_T is the measured tropospheric value in year n, $(n-1)$, . . . , and so on. Because the biospheric ^{14}C levels at northern latitudes are enhanced by the coincidence of the maxima for stratospheric/tropospheric mixing and carbon fixation through photosynthesis, the tropospheric (Δ_T) values used in calculation (1) were those measured for July to August of each year (Fig. 4).

From the data presented in Fig. 4 it is evident that during the decade after a major injection of ^{14}C to the atmosphere the correlation between the specific activity of ^{14}C in man and that in his immediate environment is complex. Apart from the uncertainty in computation of the mean biospheric ^{14}C enrichment it seems from the nature of the divergence, particularly during the past five years, that other factors are significant in determining the ^{14}C level in body protein. The apparent lag shown in human ^{14}C relative to the calculated biospheric levels is probably a function of (i) the percentage of dietary protein derived from marine sources, (ii) the assimilation of protein imported from other latitudes of lower ^{14}C specific activity, and (iii) the mean residence time for carbon in human tissues.

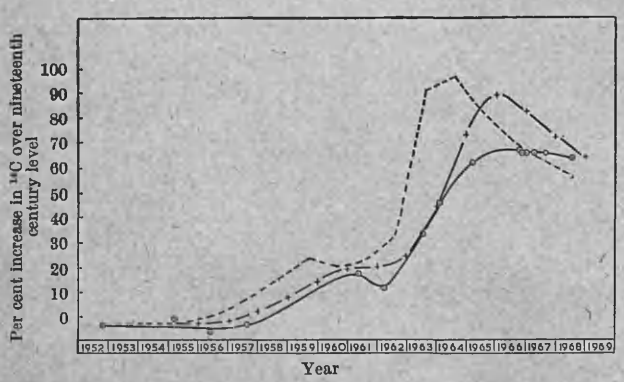

Fig. 4. ^{14}C variations in the latitude band 50°–60° N. – – –, Measured tropospheric CO_2 (July and August); +——+, estimated terrestrial biosphere; ⊙——⊙, measured blood protein carbon.

Likelihood of Errors

The possible error involved in estimates of human ^{14}C levels based on present theoretical techniques is significant only during the decade after a period of artificial ^{14}C production. In considerations of this first decade, however, it should be realized that significant errors may be incurred by acceptance of human ^{14}C levels estimated from "model" approaches. The principal source of uncertainty arises from the ill-defined function of the biospheric carbon reservoir in relation to the dynamic carbon cycle. Other significant factors include the finite time necessary for gaseous mixing within the atmospheric reservoirs and the selective nature of the human diet.

With regard to the small fraction of the total radiation dose delivered by all bomb ^{14}C produced so far, the sources and magnitude of the errors discussed may be regarded by many as negligible. This is probably so from the genetic aspect, for it appears that less than a few per cent of the total burden is delivered during the first ten years after ^{14}C production. The magnitude of the error, however, has significance in assessments of possible somatic effects caused by ^{14}C in the generation coinciding with a period of ^{14}C production[1].

The subject most susceptible to the discrepancies discussed involves the assessment of carbon transfer within the biosphere, for example, food chain or human tissue exchange studies.

Finally, should sporadic production of artificial ^{14}C continue, the possibility of compounding such errors should be borne in mind.

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GLASGOW UNIVERSITY RADIOCARBON MEASUREMENTS II

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INTRODUCTION

A third radiocarbon counting system has been established in the Chemistry Department, University of Glasgow, since April, 1968. Operating conditions for the previous systems have remained essentially as described by Baxter et al. (1969).

The counting assembly was supplied by Johnston Laboratories Inc., Baltimore and consists of 2.6ℓ internal gas counter and a concentric multiple anode anticoincidence meson detector. The counters are encased in a 4-in.-thick shield manufactured from aged lead by J. Girdler and Co., London.

CO_2 is employed as the counting gas at a constant filling pressure of 760 mm. Hg at 15°C. Operational parameters are as follows: (1) anticoincidence plateau: greater than 800 v long with slope less than 0.5% per 100 v; (2) detector operating voltage: 3.48 ± 0.05 Kv. Adjustment is made within this range to ensure identical gas gain for all gases counted; (3) detector background count rate: 5.53 ± 0.12 (± 2σ) counts/min. at 1013 mbar. A linear variation of background count rate with barometric pressure, amounts to -0.01 count/min./mbar; (4) net activity of NBS oxalic acid modern standard: 14.37 ± 0.08 (± 2σ) counts/min., after correction for fractionation and decay.

CO_2 samples are normally stored for 14 days prior to counting to allow for radon decay. The presence of radon, however, is monitored via energy discrimination during each counting sequence. When necessary, a correction is applied to the total count rate to allow for the contribution of radon and its beta active daughter products.

Samples are counted at least twice and several days apart to give a minimum total of 60,000 counts. Modern standard and background activities are monitored weekly to check counter performance.

Mass spectrometric analysis for fractionation correction have been performed at The National Physical Laboratory, Teddington.

Calculations are based on the Lamont VIII formulae (Radiocarbon 1961, v. 3, p. 176-204) and errors arising from uncertainties in C^{14} measurement are quoted to one standard deviation (1σ).

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e National Physical Laboratory has again cooperated in providing facilities for C^{13}/C^{12} measurement. Mrs. M. Currie provided excellent technical assistance in the laboratory.

SAMPLE DESCRIPTIONS

I. INTERCALIBRATION SAMPLES

Prior to routine measurement of C^{14} activities with the new system intercalibration was performed in conjunction with the established radiocarbon counting facilities at Glasgow (Baxter et al., 1969).

GU-67. Kilphedir hut circles, Sutherland, Scotland 1922 ± 60 A.D. 28

Charcoal. Comment: sample previously described and reported under GU-10, 1908 ± 60, GU-11, 2064 ± 55 and L-1061, 2100 ± 80.

Atmospheric CO_2 samples, counted as CO_2 and then converted to CH_4 for measurement on alternative counting systems. Coll. by Central Electricity Generating Board at Cwm Dyli, Mt. Snowdon, Wales, alt. 300ft (53°03' N lat, 04°00' W long).

Snowdon, Wales 1968	δC^{14}‰	δC^{13}‰	Δ‰
GU-83	60.0 ± 0.9	-21.3	58.9 ± 0.9
CO_2 coll. April 1968. Counted as CO_2 on new system.			
GU-68	59.8 ± 0.7	-21.3	58.7 ± 0.8
CO_2 coll. April 1968. Counted as CH_4 on system 1.			
GU-69	60.5 ± 1.1	-21.3	59.4 ± 1.2
CO_2 coll. April 1968. Counted as CH_4 on system 2.			

	δC^{14}‰	δC^{13}‰	Δ‰
GU-70	61.6 ± 0.9	-20.5	60.2 ± 0.9

CO_2 coll. June 1968. Counted as CO_2 on new system.

GU-71	60.0 ± 0.7	-20.5	58.7 ± 0.8

CO_2 coll. June 1968. Counted as CH_4 on system 1.

... Agreement between systems is satisfactory; no further designation of counting system is deemed necessary.

II. ATMOSPHERIC CO_2 SAMPLES

(A) Ground level

Data reported here are derived from atmospheric CO_2 samples coll. at various sites in the U.K. and throughout the world. Measurements were made as part of 2 continuing research programs, viz., (a) C^{14} concentrations in humans in relationship to those of their immediate environment (Harkness and Walton, 1969) and (b) transport of C^{14} within the "dynamic" carbon reservoir (Walton et al. 1969).

CO_2 coll. by exposure of carbonate free 8N KOH solution to atmosphere for each calendar month.

Snowdon series, 1967

CO_2 coll. by the Central Electricity Generating Board in a ventilated cabinet at Cwm Dyli Power Sta. on E slope of Mt. Snowdon (53° 03' N Lat, 04° 00' W Long).

Snowdon series 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-72	May	64.4 ± 0.8	-19.9	62.7 ± 0.8
GU-73	June	54.0 ± 0.9	-18.1	51.8 ± 1.0

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-74	July	64.8 ± 1.5	-17.4	62.2 ± 1.6
GU-75	Aug.	60.0 ± 0.6	-22.8	59.3 ± 0.7
GU-76	Sept.	62.1 ± 0.8	-17.8	59.8 ± 0.8
GU-77	Oct.	59.8 ± 0.6	-18.0	57.6 ± 0.7
GU-78	Nov.	59.1 ± 0.8	-20.2	57.6 ± 0.8
GU-79	Dec.	54.3 ± 1.4	-18.3	52.2 ± 1.5
Snowdon series, 1968				
GU-80	Jan.	58.5 ± 1.4	-21.4	57.3 ± 1.5
GU-81	Feb.	52.9 ± 1.3	-21.6	51.9 ± 1.4
GU-82	March	57.1 ± 1.4	-20.7	55.8 ± 1.5
GU-83	April	60.0 ± 0.9	-21.3	58.9 ± 0.9
GU-84	May	60.3 ± 0.8	-20.5	58.8 ± 0.9
GU-85	June	61.6 ± 0.8	-20.5	60.2 ± 1.0
GU-86	July	61.9 ± 0.9	-20.6	60.5 ± 1.0
GU-87	Aug.	56.0 ± 1.0	-20.0	54.4 ± 1.1
GU-88	Sept.	59.3 ± 1.0	-20.4	57.8 ± 1.1
GU-89	Oct.	55.8 ± 1.4	-19.9	54.9 ± 1.4
GU-90	Nov.	54.9 ± 1.2	-21.5	54.0 ± 1.3
GU-91	Dec.	50.7 ± 0.9	-22.9	50.0 ± 1.0
Snowdon series, 1969				
GU-92	Jan.	57.5 ± 1.3	-21.6	56.5 ± 1.4
GU-93	Feb.	55.1 ± 0.8	-24.5	55.0 ± 0.9
GU-95	April	57.4 ± 0.7	-21.2	56.2 ± 0.8

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-96	May	57.9 ± 0.8	-20.3	56.4 ± 0.9
GU-97	June	52.4 ± 0.8	-19.2	50.7 ± 0.9
GU-98	July	56.8 ± 0.8	-21.4	55.7 ± 0.8
GU-99	Aug.	54.9 ± 0.8	-19.5	53.2 ± 0.9

Comment: sampling station is remote from any source of fossil fuel CO_2 or possible contamination by $C^{14}O_2$ from nuclear establishments. A seasonal variation in the tropospheric C^{14} concentration is evident, and is in agreement with present theories of stratospheric/tropospheric mixing patterns.

Chilton, England series

CO_2 coll. by the United Kingdom Atomic Energy Comm. at a site adjacent to A.E.R.E. Harwell (51° 31' N Lat, 01° 20' W Long).

Chilton series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-100	May	78.2 ± 0.9	-24.0	77.2 ± 1.0
GU-101	June	70.8 ± 0.8	-22.1	69.8 ± 0.9
GU-102	July	67.3 ± 0.4	-20.3	65.8 ± 0.6
GU-103	Aug.	60.3 ± 1.6	-24.7	59.3 ± 1.7
GU-104	Sept.	68.0 ± 0.8	-21.1	66.8 ± 0.8
GU-105	Oct.	61.0 ± 0.8	-25.3	60.1 ± 1.0
GU-106	Nov.	58.2 ± 1.0	-22.9	57.5 ± 1.2
GU-107	Dec.	62.8 ± 1.2	-22.5	61.8 ± 1.2

Chilton series, 1968

Sample No.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-108	Jan.	54.8 ± 1.4	-25.1	54.9 ± 1.4
GU-109	Feb.	49.6 ± 0.5	-24.9	48.7 ± 0.6
GU-110	March	57.3 ± 1.0	-22.0	56.3 ± 1.0
GU-111	April	62.5 ± 0.9	-25.5	62.6 ± 1.0
GU-112	May	63.0 ± 0.9	-21.3	61.8 ± 1.0
GU-113	June	63.5 ± 0.9	-21.0	62.2 ± 1.0
GU-114	July	61.0 ± 1.3	-24.6	60.9 ± 1.4
GU-115	Aug.	60.3 ± 1.3	-23.4	59.7 ± 1.4
GU-116	Sept.	63.4 ± 1.1	-24.1	63.1 ± 1.2
GU-117	Oct.	79.9 ± 1.4	-25.6	80.1 ± 1.5
GU-118	Nov.	52.3 ± 1.2	-26.4	52.8 ± 1.3
GU-119	Dec.	49.2 ± 1.1	-22.4	48.5 ± 1.2
Chilton series, 1969				
GU-120	Jan.	65.7 ± 0.8	-25.6	65.9 ± 0.9
GU-121	Feb.	55.1 ± 0.8	-29.4	56.5 ± 0.9
GU-122	March	55.1 ± 0.9	-25.5	55.3 ± 1.0
GU-123	April	64.8 ± 0.8	-24.7	64.7 ± 0.8
GU-124	May	56.9 ± 0.7	-24.5	56.8 ± 0.7
GU-125	June	73.6 ± 0.8	-22.8	72.6 ± 0.9
GU-126	July	59.2 ± 0.8	-22.9	58.5 ± 0.9
GU-127	Aug.	71.0 ± 0.8	-23.6	70.6 ± 0.9

Comment: occasional high C^{14} concentrations would appear to indicate localized atmospheric contamination from adjacent nuclear establishment (ca. 2km away). A study of the above data relative to prevailing wind direction at sampling site is being made to clarify this possibility.

Lerwick, Scotland series

Samples coll. by Meteorologic Office in their ventilated East hut, Lerwick (60° 08' N Lat, 01° 11' W Long).

Lerwick series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-128	Nov.	65.0 ± 1.1	-22.6	64.2 ± 1.2
Lerwick series, 1968				
GU-129	Jan.	62.4 ± 1.2	-21.2	61.1 ± 1.2
GU-130	April	68.1 ± 1.2	-22.7	67.3 ± 1.3
GU-131	July	64.0 ± 0.9	-18.4	61.8 ± 1.0
GU-132	Oct.	58.8 ± 1.0	-19.9	57.2 ± 1.0

Victoria, B.C. series

Samples coll. by Defence Research Establishment Pacific, Canada, in covered box with gauze sides to allow free circulation of air (48° 25' N Lat, 123° 19' W Long).

Victoria series 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-133	Jan.	60.4 ± 0.8	-18.4	58.3 ± 0.9

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-134	April	63.9 ± 0.9	-17.6	61.5 ± 0.9
GU-135	July	65.1 ± 0.9	-18.3	62.9 ± 1.0
GU-136	Oct.	59.4 ± 0.8	-18.0	57.1 ± 0.9
Victoria series 1968				
GU-137	Jan.	58.4 ± 0.9	-20.7	57.0 ± 1.0
GU-138	April	68.4 ± 1.0	-21.9	67.4 ± 1.1
GU-139	May	66.0 ± 1.0	-20.2	64.4 ± 1.1
GU-140	Sept.	53.5 ± 0.9	-21.8	52.6 ± 1.0
GU-141	Dec.	53.0 ± 1.0	-21.5	51.9 ± 1.0

Gibraltar series

Samples coll. by Meteorologic Office, R.A.F. Gibraltar, in well-ventilated room, adjacent to open window (36° 09' N Lat, 05° 21' W Long).

Gibraltar series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-142	Sept.	64.9 ± 1.1	-19.0	62.9 ± 1.2
GU- 143	Nov.	69.1 ± 1.6	-21.6	68.0 ± 1.7
Gibraltar series, 1968				
GU-144	Jan.	67.8 ± 0.8	-20.1	66.2 ± 0.9
GU-145	April	57.4 ± 1.1	-20.4	56.0 ± 1.2
GU-146	July	52.6 ± 0.9	-23.2	52.0 ± 1.0
GU-147	Oct.	67.0 ± 1.1	-22.3	66.1 ± 1.2
GU-148	Nov.	54.0 ± 1.2	-21.2	52.9 ± 1.3

ong Kong series

Samples coll. by Meteorologic Office at Tates Cairn radar sta. in Stevenson screen which shelters samples from both rain and dry deposition (22° 18' N Lat, 14° 10' E Long).

Hong Kong series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-149	Jan.	60.4 ± 0.9	-26.3	60.8 ± 1.0
GU-150	April	61.2 ± 0.9	-25.5	61.3 ± 0.9
GU-151	July	55.2 ± 0.8	-26.2	55.6 ± 0.9
GU-152	Nov.	51.1 ± 1.0	-27.0	51.7 ± 1.1
Hong Kong series, 1968				
GU-153	Jan.	54.0 ± 1.1	-28.1	55.0 ± 1.2
GU-154	April	56.6 ± 1.0	-26.2	56.9 ± 1.1
GU-155	July	52.6 ± 1.1	-21.4	51.5 ± 1.2
GU-156	Nov.	54.7 ± 1.0	-24.4	54.5 ± 1.0

Singapore series

Samples coll. by Meteorologic Office, R.A.F. Changi, Singapore, at airport (01° 22' N Lat, 103° 59' E Long).

Singapore series, 1968

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-157	Jan.	59.0 ± 0.8	-22.0	58.1 ± 0.9
GU-158	April	57.4 ± 0.8	-23.8	57.0 ± 1.0
GU-159	July	53.2 ± 1.1	-25.5	53.4 ± 1.2
GU-160	Oct.	51.1 ± 1.1	-23.6	50.7 ± 1.2

Suva, Fiji Island series

Samples coll. by Meteorologic Office in instrument hut (18° 09' S Lat, 178° 27' E Long).

Fiji Island series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-161	Jan.	61.8 ± 0.8	-18.5	59.7 ± 0.9
GU-162	April	58.1 ± 0.8	-18.9	56.2 ± 0.9
GU-163	July	58.5 ± 0.9	-18.1	56.3 ± 1.0
GU-164	Oct.	64.5 ± 1.2	-18.0	62.2 ± 1.3
Fiji Island series, 1968				
GU-165	Jan.	54.9 ± 1.1	-20.8	53.6 ± 1.2
GU-166	April	55.4 ± 0.9	-21.2	54.3 ± 1.0
GU-167	July	56.1 ± 0.9	-21.9	55.2 ± 1.0
GU-168	Oct.	54.6 ± 1.0	-21.7	53.5 ± 1.0

Pretoria series

Samples coll. by Atomic Energy Board, Pelindaba, Pretoria, in Stephenson screen housing a variety of meteorologic instruments (25° 45' S Lat, 28° 16' E Long).

Pretoria series, 1968

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-169	Jan.	59.0 ± 1.1	-23.3	58.4 ± 1.1
GU-170	April	54.2 ± 0.9	-24.8	54.2 ± 1.0
GU-171	July	51.9 ± 1.2	-21.6	50.9 ± 1.3
GU-172	Oct.	63.2 ± 1.0	-24.3	63.0 ± 1.1
GU-173	Dec.	52.5 ± 0.8	-23.6	52.1 ± 0.9

lbourne series

Samples coll. by Meteorologic Office, in thermometer screen fitted with perspex hood for protection against dry deposition (37° 49' S Lat, 144° 58' E Long).

Melbourne series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-174	Jan.	55.6 ± 0.9	-25.0	55.6 ± 1.0
GU-175	April	56.3 ± 0.8	-26.7	56.9 ± 0.9
GU-176	July	51.2 ± 1.0	-20.1	49.8 ± 1.0
GU-177	Oct.	52.3 ± 0.9	-21.4	51.2 ± 0.9
Melbourne series, 1968				
GU-178	Jan.	52.9 ± 0.8	-19.1	51.1 ± 0.9
GU-179	April/ May	50.4 ± 1.1	-20.6	49.0 ± 1.2
GU-180	July	47.2 ± 1.1	-21.7	46.3 ± 1.2
GU-181	Oct.	49.6 ± 1.1	-22.1	48.7 ± 1.2

Comment: C^{14} activities in Melbourne samples are generally low. The reason for this may be a "local" Suess effect, because there are some smoke-producing stacks within 1 mi of sampling site and the harbour is ca. 3 mi away.

Stanley, Falkland Islands series

Samples coll. outdoors by Meteorologic Office, Stanley, Falkland Is., in meteorologic thermometer screen (51° 42' S Lat, 57° 52' W Long).

anley series, 1968

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-182	Jan.	55.1 ± 1.0	-21.9	54.2 ± 1.0
GU-183	April	56.3 ± 0.8	-24.2	56.1 ± 0.8
GU-184	July	52.4 ± 0.8	-24.8	52.3 ± 0.9
GU-185	Oct.	49.0 ± 1.0	-24.7	49.0 ± 1.0

Argentine Islands series

Samples coll. by British Antarctic Survey in magnetic observatory (65° 15' S Lat, 64° 16' W Long).

Argentine Islands series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-186	April	55.4 ± 0.9	-20.4	54.0 ± 1.0
GU-187	July	53.9 ± 0.8	-20.9	52.6 ± 0.9
GU-188	Oct.	54.7 ± 0.9	-21.4	53.6 ± 0.9
Argentine Islands series, 1968				
GU-189	April	53.2 ± 0.9	(-20.9)	52.0 ± 1.0*
GU-190	Oct.	52.8 ± 0.9	(-20.9)	51.5 ± 0.9*

Comment: asterisk indicates that no mass spectrometric measurement was available for sample; a value of -20.9 ± 1‰ was assumed.

Halley Bay series

Samples coll. by British Antarctic Survey in magnetic hut during summer and in ozone hut during winter (75° 31' S Lat, 26° 45' W Long).

lley Bay series, 1967

Sample no.	Coll. date	δC^{14}‰	δC^{13}‰	Δ‰
GU-191	Dec.	55.8 ± 0.9	-20.0	54.2 ± 0.9
Halley Bay series, 1968				
GU-192	May	55.3 ± 0.9	-28.3	56.4 ± 1.0
GU-193	July	55.1 ± 1.0	-22.0	54.2 ± 1.1
GU-194	Oct.	52.2 ± 1.0	-22.9	51.6 ± 1.1

(B) Upper atmospheric samples

The following C^{14} activities were measured for CO_2 coll. from the upper troposphere and lower stratosphere during the period June 1967 to December 1968,

Sampling was confined to flight paths within the region 50° to 60° N Lat, and 1° E to 8° W Long.

Atmospheric CO_2 was adsorbed on 1/8 in. pellets of molecular sieve, Linde Type 4A, using the techniques described by Godwin and Willis (Radiocarbon, 1964, V.6, p.134). Sampling time was 20 min. and this proved sufficient for the collection of ca. 4.0ℓ - atm. CO_2, using 2 kg sieve per sample. Adsorbed CO_2 was recovered from the sieve material with steam displacement and coll. as $BaCO_3$ by absorption in $Ba(OH)_2$/KOH solution (Harkness, 1970).

Upper atmospheric CO_2

Sample no.	Coll. date	Alt.	Tropopause ht.	δC^{14}‰	δC^{13}‰	Δ‰
GU-195	30 June 1967	41,000 ft.	39,000 ft.	87.7 ± 1.4	-20.2	85.9 ± 1.6
GU-196	20 Dec. 1967	41,000 ft.	39,000 ft.	87.0 ± 1.9	-19.6	85.0 ± 2.1
GU-197	15 Jan. 1967	43,000 ft.	41,000 ft.	79.9 ± 0.9	-18.3	77.5 ± 1.0
GU-198	15 Feb. 1968	39,000 ft.	35,000 ft.	74.5 ± 0.8	-17.8	72.0 ± 0.8
GU-199	15 Feb. 1968	31,000 ft.	35,000 ft.	58.3 ± 0.7	-17.1	55.8 ± 0.7
GU-200	15 Mar. 1968	43,000 ft.	41,000 ft.	62.8 ± 2.1	-20.5	61.4 ± 2.1
GU-201	19 Mar. 1968	31,000 ft.	28,000 ft.	62.8 ± 0.9	-19.8	61.1 ± 0.9
GU-202	19 Mar. 1968	25,000 ft.	28,000 ft.	64.6 ± 0.9	-20.3	63.0 ± 1.0
GU-203	26 Mar. 1968	41,000 ft.	38,000 ft.	72.3 ± 0.8	-20.2	70.6 ± 0.8
GU-204	26 Apr. 1968	41,000 ft.	39,000 ft.	73.6 ± 0.9	-16.9	70.7 ± 0.7
GU-205	30 Apr. 1968	39,000 ft.	29,000 ft.	63.7 ± 2.2	-22.4	62.8 ± 2.2
GU-206	30 Apr. 1968	27,000 ft.	29,000 ft.	62.1 ± 0.8	-19.7	60.4 ± 0.9
GU-207	21 May 1968	39,000 ft.	34,000 ft.	79.5 ± 1.6	-21.8	78.3 ± 1.6
GU-208	4 Nov. 1968	45,000 ft.	41,000 ft.	74.8 ± 0.8	-18.9	72.7 ± 0.9
GU-209	6 Dec. 1968	41,000 ft.	39,000 ft.	72.5 ± 0.6	-20.3	70.8 ± 0.7

III. BLOOD PROTEIN SAMPLES

Data reported here are derived from the protein fraction separated from human blood plasma coll. in S. Scotland. Each sample represents a composite prepared from the whole blood of 10 donors. Collection date quoted is accurate to within ± 5 days.

Blood protein, S. Scotland

Sample no.	Sample date	δC^{14}‰	δC^{13}‰	Δ‰
GU-210	26 Oct. 1952	-3.6 ± 0.5	-28.4	-2.9 ± 0.6
GU-211	20 Sept 1953	-8.1 ± 0.6	-26.4	-7.9 ± 0.6
GU-212	1 Apr. 1954	-5.4 ± 0.7	-26.2	-5.1 ± 0.8
GU-213	23 Mar. 1955	-1.6 ± 0.5	-26.2	-1.3 ± 0.5
GU-214	5 May 1956	-7.8 ± 0.6	-29.5	-7.0 ± 0.7
GU-215	26 Sept 1957	-5.0 ± 0.7	-30.8	-3.9 ± 0.8
GU-216	11 Feb. 1960	9.1 ± 0.6	-26.5	9.4 ± 0.7
GU-217	23 May 1961	16.4 ± 0.9	-27.2	16.9 ± 1.0
GU-218	7 Apr. 1962	9.9 ± 0.9	-29.4	10.8 ± 0.9
GU-219	15 July 1963	32.0 ± 1.0	-32.3	33.9 ± 1.1
GU-220	9 Feb. 1964	44.4 ± 1.0	-29.4	45.6 ± 1.0
GU-221	5 Mar. 1965	60.1 ± 0.8	-29.5	61.5 ± 0.8
GU-222	17 Oct. 1966	65.4 ± 0.8	-27.2	66.2 ± 0.8
GU-223	15 Nov. 1966	64.0 ± 0.7	-30.0	65.6 ± 0.8
GU-224	30 Dec. 1966	64.5 ± 0.7	-27.9	65.4 ± 0.7
GU-225	8 Apr. 1967	64.2 ± 0.6	-28.4	65.3 ± 0.7
GU-226	27 Oct. 1967	62.7 ± 0.7	-33.2	65.3 ± 0.8
GU-227	10 July 1968	63.2 ± 1.0	-26.3	63.4 ± 1.0

Comment: C^{14} concentrations in blood protein indicate significant correlation with modifying influences on atmospheric C^{14} levels, viz. Suess effect and bomb effect. Blood protein C^{14} levels, however, did not reach peak concentrations attained in atmosphere, reflecting variations in source of carbon in diet and possibly tissue "turnover" time (Harkness and Walton 1969).

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